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NATIONAL NUCLEAR ENERGY SERIES
Manhattan Project Technical Section

Division VIII—Volume 1

ANALYTICAL CHEMISTRY
OF THE MANHATTAN PROJECT



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ANALYTICAL CHEMISTRY OF THE MANHATTAN PROJECT

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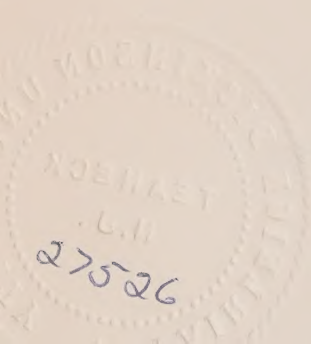
ANALYTICAL CHEMISTRY OF THE MANHATTAN PROJECT

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FOREWORD

The wartime project for development of atomic energy was a remarkable feat of cooperation and accomplishment by government, science, industry, labor, and the military services aimed exclusively at the military application of atomic energy. Our present national atomic energy program, expanding upon the previous developments, is directed not only toward the assurance of national security but also toward the realization of the immense potential benefits atomic energy holds for our civilization. The record of progress and the results of extensive scientific investigations and engineering development are contained in the National Nuclear Energy Series. This knowledge, which offers the basis of world-wide benefits from nuclear science, is being published in the established scientific tradition, not solely to meet the precise needs of science but also in support of the high goals of the American people set forth in the Atomic Energy Act. The work reported in this series is a tribute to all the scientists engaged in both the Manhattan Project and the postwar Atomic Energy Commission program.

Gordon E. Dean, Chairman
U. S. Atomic Energy Commission

ACKNOWLEDGMENT

The Manhattan Project Technical Section of the National Nuclear Energy Series embodies results of work done in the nation's wartime atomic energy program by numerous contractors, including Columbia University. The arrangements for publication of the series volumes were effected by Columbia University, under a contract with the United States Atomic Energy Commission. The Commission, for itself and for the other contractors who contributed to this series, wishes to record here its appreciation of this service of Columbia University in support of the national nuclear energy program.

PREFACE

This volume is one of a series which has been prepared as a record of the research work done under the Manhattan Project and the Atomic Energy Commission. The name Manhattan Project was assigned by the Corps of Engineers, War Department, to the far-flung scientific and engineering activities which had as their objective the utilization of atomic energy for military purposes. In the attainment of this objective, there were many developments in scientific and technical fields which are of general interest. The National Nuclear Energy Series (Manhattan Project Technical Section) is a record of these scientific and technical contributions, as well as of the developments in these fields which are being sponsored by the Atomic Energy Commission.

The declassified portion of the National Nuclear Energy Series, when completed, is expected to consist of some 60 volumes. These will be grouped into eight divisions, as follows:

- Division I — Electromagnetic Separation Project
- Division II — Gaseous Diffusion Project
- Division III — Special Separations Project
- Division IV — Plutonium Project
- Division V — Los Alamos Project
- Division VI — University of Rochester Project
- Division VII — Materials Procurement Project
- Division VIII — Manhattan Project

Soon after the close of the war the Manhattan Project was able to give its attention to the preparation of a complete record of the research work accomplished under Project contracts. Writing programs were authorized at all laboratories, with the object of obtaining complete coverage of Project results. Each major installation was requested to designate one or more representatives to make up a committee, which was first called the Manhattan Project Editorial Advisory Board, and later, after the sponsorship of the Series was assumed by the Atomic Energy Commission, the Project Editorial Advisory Board. This group made plans to coordinate the writing programs at all the installations, and acted as an advisory group in all matters affecting the Project-wide writing program. Its last meeting was held on Feb. 9, 1948, when it recommended the publisher for the Series.

The names of the Board members and of the installations which they represented are given below.

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University of Rochester	D. R. Charles, M. J. Wantman

* Represented Madison Square Area of the Manhattan District.

† The Y-12 plant at Oak Ridge was operated by Tennessee Eastman Corporation until May 4, 1947, at which time operations were taken over by Carbide & Carbon Chemicals Corporation.

‡ Clinton Laboratories was the former name of the Oak Ridge National Laboratory.

§ SAM (Substitute Alloy Materials) was the code name for the laboratories operated by Columbia University in New York under the direction of Dr. H. C. Urey, where much of the experimental work on isotope separation was done. On Feb. 1, 1945, the administration of these laboratories became the responsibility of Carbide & Carbon Chemicals Corporation. Research in progress there was transferred to the K-25 plant at Oak Ridge in June, 1946, and the New York laboratories were then closed.

Many difficulties were encountered in preparing a unified account of Atomic Energy Project work. For example, the Project Editorial Advisory Board was the first committee ever organized with representatives from every major installation of the Atomic Energy Project. Compartmentation for security was so rigorous during the war that it had been considered necessary to allow a certain amount of duplication of effort rather than to permit unrestricted circulation of research information between certain installations. As a result, the writing programs of different installations inevitably overlap markedly in many scientific fields. The Editorial Advisory Board has exerted itself to reduce duplication in so far as possible and to eliminate discrepancies in factual data included in the volumes of the NNES. In particular, unified Project-wide volumes have been prepared on Uranium Chemistry and on the Analysis of Project Materials. Nevertheless, the reader will find many instances of differences in results or conclusions on similar subject matter prepared by different authors. This has not seemed wholly undesirable for several reasons. First of all, such divergencies are not unnatural and stimulate investigation. Second, promptness of publication has seemed more important than the removal of all discrepancies. Finally, many Project scientists completed their contributions some time ago and have become engrossed in other activities so that their time has not been available for a detailed review of their work in relation to similar work done at other installations.

The completion of the various individual volumes of the Series has also been beset with difficulties. Many of the key authors and editors have had important responsibilities in planning the future of atomic energy research. Under these circumstances, the completion of this technical series has been delayed longer than its editors wished. The volumes are being released in their present form in the interest of presenting the material as promptly as possible to those who can make use of it.

The Editorial Advisory Board

The Manhattan Project Technical Section of the National Nuclear Energy Series is intended to be a comprehensive account of the scientific and technical achievements of the United States program for the development of atomic energy. It is not intended to be a detailed documentary record of the making of any inventions that happen to be mentioned in it. Therefore, the dates used in the Series should be regarded as a general temporal frame of reference, rather than as establishing dates of conception of inventions, of their reduction to practice, or of occasions of first use. While a reasonable effort has been made to assign credit fairly in the NNES volumes, this may, in many cases, be given to a group identified by the name of its leader rather than to an individual who was an actual inventor.

VOLUME EDITOR'S PREFACE

In 1944 the compilation of the analytical chemistry methods used at the installations of the Metallurgical Laboratory was begun by E. B. Ashcraft and C. R. McKinney. This work was continued under the joint editorship of L. L. Quill and J. I. Watters. At about the same time, similar scientific records were also started at other Project sites than those of the Metallurgical Laboratory.

In February, 1945, the Manhattan District Analytical Committee was founded to consider and review analytical chemistry problems of the Project; C. J. Rodden was chairman of the group. This committee, in January, 1946, agreed that information concerning the analytical chemistry used on the entire Project should be published as a separate entity; this was thought more desirable than publication of separate volumes from the various installations, because in this manner the over-all picture would be more clearly presented.

The outline of the Metallurgical Laboratory was expanded to cover the entire Project work. T. D. Price was designated as the Editorial Chairman, and served from January to June, 1946. Under his direction, the final outline was prepared. The various representatives on the Committee undertook to write, or have written, certain of the chapters with which they were more familiar. In June, 1946, C. J. Rodden was designated to serve as Editor-in-Chief.

The Manhattan Project Analytical Committee has consisted of the following members who have served at one time or another:

National Bureau of Standards, Washington, D. C.	C. J. Rodden, Chairman
Carbide & Carbon Chemicals Corporation, Oak Ridge, Tenn.	H. F. Priest, E. Staple, R. H. Wiswall
Carbide & Carbon Chemicals Corporation, SAM Laboratories, New York	G. M. Murphy, F. E. McKenna
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Mallinckrodt Chemical Works, St. Louis, Mo.	A. Q. Butler
Manhattan Project, Oak Ridge, Tenn.	P. Aebersold, D. D. Wright, A. F. Thompson
Metallurgical Laboratory, University of Chicago, and associated laboratories	L. L. Quill, J. I. Watters

Monsanto Chemical Company, Clinton Laboratories, Oak Ridge, Tenn.	G. E. Boyd, L. B. Rogers
Princeton University, Princeton, N. J.	N. H. Furman
University of California, Radiation Laboratory, Berkeley, Calif.	E. H. Huffman
University of Rochester, Rochester, N. Y.	J. I. Flagg

The scientific personnel who contributed to the writing and editing of the individual chapters and who are not otherwise acknowledged are:

S. W. Sheel	Metallurgical Laboratory	Chap. 8
D. Revinson	Metallurgical Laboratory	Chap. 12
B. W. Lewis	Metallurgical Laboratory	Chap. 21
C. R. Schwob	Metallurgical Laboratory	Chap. 22
G. A. Cowan	Metallurgical Laboratory	Chaps. 22, 24
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 University of Rochester, Rochester, N. Y.

James I. Hoffman of the National Bureau of Standards, by acting as responsible reviewer, aided materially in the declassification of the individual chapters.

Alberto F. Thompson of the Atomic Energy Commission contributed by his aid and enthusiasm to the final publication of the volume.

The volume was made possible not only by the scientific contributors but also by the personnel at the many sites who handled typing, copy checking, duplicating, preparation of illustrations, working card files, and correspondence necessary to assemble the material. The following persons contributed greatly to the work: R. C. Maloney of the National Bureau of Standards; M. P. Stutts, S. A. Rice, V. Elkins, R. Keel of the Atomic Energy Commission; and J. A. Ruthven of Carbide & Carbon Chemicals Corporation.

Clement J. Rodden

PUBLISHER'S NOTE

Although every effort has been made to ensure accuracy in references, at the time of publication of this book some of the other volumes of the Series had not been completed. It is therefore possible that some of the references to other volumes are in error. It is hoped that the extensive cross checking which has been done in the preparation of this volume has resulted in keeping such errors to a minimum.

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INTRODUCTION

The necessity for high chemical purity of many of the materials used for the production of atomic energy was recognized in the early stages of the Project.

The development of analytical chemical methods was one of the earliest problems on the Project. The first materials to be examined were uranium oxides, uranium metal, and graphite. In a short time, as the Project developed, it was necessary to analyze for nearly all the elements of the periodic system in all types of materials.

The methods that were developed were in the majority of cases based on those previously published and in many cases were but adaptations for specific purposes. Because of the necessary compartmentation, duplication was inevitable. It is recognized that the methods described in many cases could be improved, but, owing to wartime stress, time was not available to make a more thorough investigation. The methods used served the purpose for which they were intended. Considerable advancement has been made in the determination of uranium in many types of materials. The determination of traces of many elements was investigated, and improvements were made in methods in many instances.

This volume is a compilation of the methods used for the analysis of many kinds of materials used on the Project. It does not include all available published methods for the determination of the elements in question. On the other hand, references have been included to certain methods that were used even though they are well known and antedate the Project.

The emphasis is on the analysis of materials that were of particular interest, such as uranium and its compounds, plutonium and its compounds, and thorium and its compounds. In this volume radiochemical methods have been but superficially covered since the subject is treated in detail in Division IV, Volume 9, of the National Nuclear Energy Series.

This volume is divided into two parts. Part I is concerned with the determination of individual elements, and Part II deals with general instrumental methods.

Health hazards in handling Project materials are discussed in detail in Division VI, Volume 1, of the National Nuclear Energy Series.

Many excellent devices for monitoring radiations have been constructed; these are described in Division IV, Volume 8 A, of this series. Monitoring on individuals may employ photographic x-ray film, carried by the individual, which after development indicates the extent of beta-ray, gamma-ray, or neutron exposure. Small "pencil" ionization chambers may also be carried to record radiation exposure.

Part I

ANALYTICAL CHEMISTRY OF ELEMENTS STUDIED
ON THE MANHATTAN PROJECT

Chapter 1

URANIUM

By C. J. Rodden and J. C. Warf*

In this chapter the methods for separating and determining uranium are discussed, and procedures are described. Because of the unique importance of uranium and its compounds, a section on basic chemical properties of this element is included. Methods of dissolving uranium metal and its compounds are discussed and methods of separation are given.

The most lengthy part of the chapter consists of detailed discussions of the gravimetric, volumetric, colorimetric, and fluorometric methods of determination and specific laboratory procedures.

1. THE CHEMISTRY OF URANIUM AND ITS COMPOUNDS¹

1.1 Introduction. A great variety of minerals and ores contain uranium, and these are widespread in geographical distribution. As a source of uranium the two most important minerals are pitchblende and carnotite. Pitchblende, U_3O_8 , is of igneous origin and contains variable amounts of other elements, whereas carnotite is a sedimentary mineral of granitic origin and contains potassium, vanadium, and uranium in the proportions approximately represented by the formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$. Carnotite usually occurs in sandstone admixtures.

*Special acknowledgment is made to the following for their contributions to sections with which they were identified: Sec. 1.4, "Complex Formation," J. F. Flagg; Sec. 2.2, "Precipitation," N. H. Furman; Sec. 3.2, "Gravimetric Methods," N. H. Furman; Sec. 3.3, "Volumetric Methods," M. S. Richmond; Sec. 3.5, "Fluorometric Methods," Forrest Clark. Acknowledgment is also made to C. C. Casto, D. P. Krause, H. F. Priest, L. B. Rogers, R. H. Smellie, D. H. Templeton, and J. I. Watters.

Uranium metal has a melting point of approximately 1130°C and a density of 18.95. It may be machined, hot-drawn, and cold-worked. The surface takes a high polish but slowly tarnishes in air.

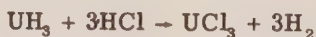
Uranium forms intermetallic compounds with most other metals; these include iron, lead, and mercury. The metal, which lies near beryllium or aluminum in electropositivity, is a strong reducing agent, and it forms binary compounds with most other elements. In the dry state compounds in which the valence of uranium is +3, +4, +5, or +6 are well known. However, in aqueous solution, uranium(V) disproportionates into uranium(IV) and uranium(VI), whereas the strong reducing agent uranium(III) is rapidly oxidized by dissolved oxygen and also slowly reduces water to liberate hydrogen. Uranium(VI), the most stable form in aqueous solution, usually exists in, and is separated from, acidic or neutral solutions as the uranyl ion, $[\text{UO}_2]^{++}$. Uranium(VI) often separates from alkaline solutions as the diuranate, $[\text{U}_2\text{O}_7]^{--}$, as, for example, $(\text{NH}_4)_2\text{U}_2\text{O}_7$. It may also separate as the uranate, $[\text{UO}_4]^{--}$, as, for example, Na_2UO_4 . Variable amounts of hydrous oxide may also be present in such precipitates.

The common uranyl salts as well as their solutions are brilliant yellow in color. Uranium(IV) salts and their solutions are deep green by reflected light. Trivalent uranium salt solutions are reddish purple, although the solid crystals may be olive-green, reddish brown, or black depending on the crystal size. The uranium (VI)/(IV) couple exhibits the Becquerel effect, in which the potential of the electrode increases with illumination. The photochemical reduction of the uranyl ion to the uranium(IV) ion by organic compounds has been the subject of considerable research.

The uranyl ion exhibits a green-yellow fluorescence, which is weak in aqueous solution but strong in the crystalline state.

Important binary compounds include the hydride, carbides, nitrides, oxides, and halides.

The hydride, a pyrophoric dark-gray powder, is formed by the action of hydrogen on the metal at 250°C at atmospheric pressure. Uranium hydride serves as a starting material for the preparation of many compounds. For example, uranium trichloride is readily prepared by the action of hydrogen chloride.



Decomposition of the hydride leaves the finely divided metal in an exceedingly reactive state. The hydride forms "amalgams" of various compositions, some of which are semisolids.

The three carbides, UC, U_2C_3 , and UC_2 , form high-melting crystals of metallic luster.

The nitrides, UN and others with composition between $\text{UN}_{1.5}$ and $\text{UN}_{1.8}$ (depending on the temperature), are unreactive dark powders. The UN is not decomposed when heated to 2500°C in an inert crucible at low pressures.

The common oxides of uranium are UO_2 , a dark-brown powder called "brown oxide"; U_3O_8 , ordinarily a black but sometimes an olive-green powder, called "black oxide"; and UO_3 , the color of which varies from red to yellow, depending on the crystal modification. Uranium peroxide, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, which is yellow, can be precipitated in slightly acidic solution by hydrogen peroxide. It dissolves in alkalis, yielding peruranates. Hydrous uranyl oxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$, dissolves easily in acids, and UO_3 and U_3O_8 are soluble in nitric acid.

There are five fluorides of uranium— UF_3 , a black-colored salt; UF_4 , a difficultly soluble compound, commonly called "green salt"; U_2F_9 , which is black; UF_5 , a white substance; and UF_6 , a colorless compound, which is readily volatile (b.p. 56.4°C). UF_4 and UF_6 are important compounds of uranium. The latter is readily hydrolyzed by water, forming uranyl fluoride. The tetrafluoride is usually prepared from the dioxide and anhydrous hydrogen fluoride at 500 to 600°C .

Uranium forms four chlorides— UCl_3 , which is olive-green; UCl_4 and UCl_5 , which are green; and UCl_6 , which is yellow. The trichloride forms a wine-red unstable solution, and the tetrachloride forms a clear green solution in water. On dissolving in water the pentachloride disproportionates, forming uranium(IV) and uranium(VI), whereas the hexachloride hydrolyzes to UO_2Cl_2 . The two higher chlorides are volatile and unstable; the tetrachloride can be sublimed at 550 to 600°C . The tribromide and tetrabromide, triiodide and tetraiodide, and mixed halides are known.

The most common uranyl salts, namely, the nitrate, sulfate, chloride, acetate, and perchlorate, are soluble yellow-colored salts. The diuranates, such as $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{Na}_2\text{U}_2\text{O}_7$, are insoluble. Various uranium(IV) salts such as the sulfate, chloride, bromide, and oxalate are readily prepared. Most of the uranyl and uranium(IV) salts form several hydrates.

Uranyl nitrate is of particular importance because, although highly ionized, it can be extracted from a concentrated nitrate solution by organic solvents such as ether. Advantage is taken of this unique property in the separation or purification of uranium.

1.2 Valence States. The oxidation potentials of the principal valence states of uranium, namely, uranium(III), uranium(IV), and uranium(VI), as well as the transitory uranium(V), are discussed in Chap. 25 on "Electrometric Methods." Owing to the relatively low oxidation potential of the uranium (VI)/(IV) couple, the element can be quantitatively converted to either valence state at will. The alter-

nate use of both valence states permits many separations not otherwise possible. An important application is the use of cupferron, which forms an extractable precipitate with uranium(IV). Other cupferrates may first be separated from the oxidized solution, and then uranium(IV) cupferrate may be precipitated alone after reduction. The same principle is sometimes used in precipitation with oxalic acid. Uranium(IV) oxalate is insoluble, but uranyl ion forms a soluble complex with oxalic acid. Titrations usually involve a prereduction to uranium(IV) followed by an oxidation titration to uranium(VI). The instability of uranium(III) has not permitted the use of this valence state in quantitative analysis.

Acidified uranyl salt solutions are readily reduced by a number of metals or their amalgams, including zinc, aluminum, magnesium, cadmium, bismuth, silver, and copper. In most cases the uranium is reduced to a mixture of the trivalent and quadrivalent states; the proportion of the former ranges up to 40 per cent of the total uranium.² Reduction of acidic chloride solutions with silver yields only the quadrivalent form. Uranyl solutions may also be reduced electrolytically to mixtures of uranium(IV) and uranium(III). Under the proper conditions tin(II) chloride, titanium(III) salts, and sodium hyposulfite reduce uranyl salts.

Trivalent uranium is a powerful reducing ion; exposure to air for a few minutes serves to oxidize it quantitatively to the quadrivalent state. Uranium(IV) solutions are relatively stable in the presence of air. When warmed to 60 to 80°C or when shaken with oxygen, they are oxidized more rapidly. Uranium(IV) in solution is converted to uranium(VI) by most of the common oxidizing agents.

A detailed description of uranium and its compounds is given in "Uranium Chemistry," National Nuclear Energy Series, Division VIII, Volume 5.

1.3 Solution of Uranium and Its Compounds. The method to be selected for the solution of metallic uranium, its alloys, or its compounds depends on the nature of the sample, the constituent to be determined, and the method of analysis. Nitric acid is often employed because it dissolves all or nearly all compounds and alloys of uranium. The presence of nitrates, however, cannot be tolerated in many procedures, such as the volumetric determination following a reduction by zinc. A general discussion of available methods of solution appears below. Methods for dissolving ores and rocks will be found under Sec. 4 of this chapter.

(a) Uranium and Its Alloys. The pure metal dissolves in nitric acid at a moderate rate and forms uranyl nitrate. Uranium turnings, sintered or pressed powder, or other forms with a large surface area,

may be oxidized explosively by nitric acid. For this reason, when large quantities are to be dissolved, only small portions (3 to 6 g at a time) should be added to the acid. The use of insufficient nitric acid in the solution results in the formation of traces of hydrazine or other intermediates³ that can be destroyed by oxidation with dichromate or permanganate.⁴

Uranium reacts extremely rapidly with 12N HCl. In 6N acid the reaction is still rapid, but 2N acid attacks the metal slowly. The reddish-violet color of trivalent uranium chloride is visible shortly after the reaction begins, but it is soon masked by a black precipitate that has a tendency to remain in suspension. The proportion of the uranium that is converted to the insoluble precipitate varies from 0.1 to 20 per cent, depending on the acid concentration, ratio of acid to metal, time of reaction, and temperature.^{5,6} The resulting mixture of black precipitate and uranium trichloride and tetrachloride can be oxidized to a clear uranyl solution by nitric acid, hydrogen peroxide, bromine water, or perchloric acid. With perchloric acid the solution must be boiled to fumes. Hydrochloric acid containing traces of fluosilicic acid dissolves uranium without the formation of the black precipitate, producing green uranium(IV) chloride.⁷

Dilute sulfuric acid has little effect on uranium. Addition of an oxidizing agent such as hydrogen peroxide causes a slow reaction. The metal can also be dissolved anodically in sulfuric acid by using a current of 1.5 amp and a potential of about 3 volts.⁸ The action of dilute perchloric acid on uranium is comparable to that of sulfuric acid in that there is scarcely any reaction except in the presence of oxidizing agents such as peroxides or chlorates. When perchloric acid is boiled down to fumes in the presence of uranium, an extremely vigorous and probably dangerous reaction takes place, during which sparks are observed.

Cold 85 per cent phosphoric acid attacks uranium slowly, but after the acid is concentrated by boiling, a fairly rapid reaction occurs. With an excess of acid a green solution of uranium(IV) phosphate is obtained which gives a gelatinous precipitate on dilution. A glassy substance, which is extremely difficult to redissolve, is formed when the solution is boiled down too far. The solution of uranium in phosphoric acid is accelerated by oxidizing agents such as nitric acid or peroxides, or by anodic oxidation.

Organic acids are in general without effect on uranium except in the presence of hydrogen chloride as a catalyst. Thus glacial acetic acid reacts to yield uranium(IV) acetate if hydrogen chloride is bubbled in, or if a little hydrochloric acid is added.⁹

Alkaline solutions of peroxides dissolve uranium and many of its compounds, forming peruranates.¹⁰

The reduction of heavy metal salts, such as mercuric nitrate, silver nitrate, stannous chloride, and platinum chloride, in aqueous solution by uranium was observed in 1882 by C. Zimmermann.¹¹ Silver sulfate solution reacts slowly with the metal. Silver perchlorate reacts vigorously, resulting in the formation of silver, silver chloride, and uranyl perchlorate.^{12,13} Cupric ammonium chloride or acetate dissolves uranium without permanent precipitation of metal.^{14,15}

The alloys of uranium can usually be dissolved as readily as uranium metal itself. Some alloys, however, are more readily dissolved; for example, uranium-lead and uranium-bismuth alloys react with water. Uranium-copper, uranium-zinc, and other alloys dissolve readily in nitric acid, but the tin alloy reacts, leaving a precipitate of hydrated stannic oxide. The columbium, tantalum, and tungsten alloys require special treatment. The nature of the alloying metal usually suggests the proper method of solution, and difficulties at this stage are rarely encountered.

(b) Uranium Oxides: Uranates. Nitric acid dissolves all the normal oxides of uranium— UO_2 , U_3O_8 , UO_3 —with the formation of uranyl nitrate. Uranium peroxide, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, is readily dissolved in an acidic reducing solution; in hydrochloric acid, uranyl chloride and chlorine are formed. The uranates, diuranates, and uranium trioxide dissolve in the common acids. Neither UO_2 nor U_3O_8 dissolves in dilute hydrochloric or sulfuric acid at a practical rate.^{16,17} Each is slowly oxidized by long heating with sulfuric acid, forming uranyl sulfate. The oxides are readily dissolved by fuming with perchloric acid, which results in the formation of uranyl perchlorate. Soluble peruranates are obtained by treatment of uranium oxides with alkaline peroxides.^{10,18}

(c) Uranium Fluorides. Uranyl fluoride and uranium hexafluoride are soluble in water. The latter is violently hydrolyzed, forming uranyl fluoride and hydrofluoric acid. Uranium pentafluoride disproportionates and hydrolyzes in water to form hydrofluoric acid, soluble uranyl fluoride, and insoluble uranium(IV) fluoride. Uranium(IV) fluoride and uranium(III) fluoride are both insoluble in water.

Uranium fluorides are often converted into U_3O_8 prior to their solution. This conversion can be accomplished by hydrolysis with steam¹⁹ or fusion with boric acid,²⁰ ammonium oxalate,²¹ or potassium pyrosulfate.²² Uranium tetrafluoride can be readily converted to U_3O_8 by ignition in air²³ or by heating with ammonium carbonate⁴⁵⁷ and then dissolved as above. Uranium tetrafluoride is readily dissolved by boric acid solutions that have been acidified with sulfuric, hydrochloric, or perchloric acid, giving uranium(IV) sulfate, chloride, or perchlorate. When a mixture of nitric and boric acids is used uranyl nitrate and fluoboric acid are formed. Ferric iron oxidizes UF_4 to

uranyl compounds and forms a complex with the fluoride ion. Aluminum chloride dissolves UF_4 by complexing the fluoride ion.²⁴ Neutral oxalate solutions dissolve uranium tetrafluoride owing to the stability of the uranium(IV) oxalate complex in neutral mediums. Strongly acidic solutions of ceric sulfate oxidize uranium tetrafluoride to uranyl fluoride. Alkaline peroxides dissolve uranium tetrafluoride and form peruranates. Uranium tetrafluoride is readily dissolved by fuming perchloric acid to form uranyl perchlorate; the hydrofluoric acid is expelled. Long boiling with nitric acid causes slow solution of uranium tetrafluoride, and heating with phosphoric acid results in the formation of uranium(IV) phosphate and removal of the fluorine. Hot concentrated sulfuric acid reacts to form a sulfate that dissolves on dilution with water. However, the fluorine is not quantitatively expelled. Treatment with dilute sulfuric acid and powdered quartz yields fluosilicic acid and uranous sulfate. Uranium trifluoride undergoes reactions similar to those of the tetrafluoride with the exception that the trifluoride is not soluble in neutral oxalates.

(d) Other Uranium Compounds. Since uranium chlorides, bromides, and iodides either dissolve in water or react with water, their solution is generally simple. Uranium carbides dissolve on prolonged boiling with nitric acid but are usually oxidized by air or oxygen to U_3O_8 before solution. Uranium sulfates, acetates, and many other salts are soluble in water.

1.4 Complex Formation. Uranium forms compounds that may be classified as double salts. The element also forms compounds that are definitely "complex." Many of these are of the "inner complex" or "chelate" type.

There are a great many good analytical data available on the composition of many of the uranium complex compounds. There is still a lack of definite evidence for the formulas for some of the complex ions in solution. Consequently, considerable caution must be observed in the interpretation of the formulas of uranium complexes for which the evidence is still indefinite.

The importance of complex ions in the analytical chemistry of uranium lies in their solubility, making them useful in separations, or in their color, making them useful in colorimetric determinations. Some different types of uranium complexes are cited in the following sections to indicate the general nature of the complex-forming power of the uranium atom.

(a) Inorganic Complexes of Uranium(VI). Many complexes of the uranyl ion with inorganic substances are known. Among the halide complexes are found the crystalline salts of fluorides such as $[\text{UO}_2\text{F}_3]^-$, $[\text{UO}_2\text{F}_5]^{-3}$, and $[\text{UO}_2\text{F}_6]^{-4}$. The formation of complexes of this type may

depend, among other things, on the ratio in which the components are mixed. Salts of the chloride anion, $[\text{UO}_2\text{Cl}_4]^{--}$, are also known, and similar complexes with the other halides probably exist.

The nitrate ion forms complexes with the uranyl ion; crystalline ammonium derivatives and potassium derivatives of $[\text{UO}_2(\text{NO}_3)_3]^-$ and $[\text{UO}_2(\text{NO}_3)_4]^{--}$ are known.

The sulfate ion forms complexes in which either two or three sulfate ions are attached to a single uranyl ion. Disulfates of potassium, $\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, and also of organic bases such as ethylene diamine and guanidine are known. The trisulfate series includes compounds such as $\text{Na}_4\text{UO}_2(\text{SO}_4)_3$. The sulfate complex apparently inhibits the precipitation of UO_4 at a pH of 1.5; the amount of interference is roughly a linear function of the sulfate concentration when the ratio of sulfate to uranyl is greater than 1.²⁵ Sulfate ion also reduces the solubility of uranyl nitrate in ether, which may be a related effect.²⁶

The carbonate complexes, formed by action of ammonium or alkali carbonates or bicarbonates on uranyl hydroxide, alkali uranates, etc., are well known and have been used for many years in analyses of uranium-bearing material.²⁷ Three molecules of carbonate are associated with each molecule of UO_2 , and the complex is an anion of the form $[\text{UO}_2(\text{CO}_3)_3]^{-4}$. However, when ammonium diuranate is dissolved in ammonium carbonate, a slight excess of carbonate over the theoretical three molecules is required.²⁸ Although the ammonium salt of the complex is soluble, the barium salt, $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3$, is insoluble.²⁹

Ammonium diuranate cannot be precipitated from ammoniacal carbonate solution by ammonium hydroxide; however, sodium diuranate can be precipitated completely from carbonate solution by sodium hydroxide. Ammonium diuranate dissolves in ammonium carbonate at about pH 7.4; if this solution is treated with hydrochloric acid, however, a precipitate of ammonium diuranate appears at pH 5.2.²⁸

Polarographic studies indicate that the same complex of the uranyl ion is present in both carbonate and bicarbonate mediums.³⁰ Electrical transport data lead to the same conclusion. These same studies also indicate qualitatively that the carbonate complex is more stable than the acetate complex, because the half-wave potential for the reduction of uranium(VI) is shifted to more negative values in carbonate or bicarbonate mediums than in the presence of acetate.

Use is made of the solubility of ammonium diuranate in ammonium carbonate in many recovery and separation reactions, particularly in the presence of iron (see references 28 and 31 to 33).

Other complexes of the uranyl ion include the cyanide, $[\text{UO}_2(\text{CN})_4]^{--}$, which has been shown by conductance measurements to exist as such

in aqueous solution. In the solid state $K_2UO_2(CN)_4$ is known.³⁴ Complex ammines of UO_2F_2 , UO_2Cl_2 , UO_2SO_4 , and $UO_2(NO_3)_2$ are known in which from two to six molecules of ammonia are held per atom of uranium. Hydroxylamine prevents the precipitation of ammonium diuranate in the separation of uranium and beryllium (or thorium).^{35,36} This may be taken as an indication of the complex formation between the hydroxylamine and the uranyl ion. Hypophosphate and pyrophosphate form soluble complexes with uranyl salts,³⁷⁻³⁹ giving compounds such as $Na_2[UO_2(HPO_3)_2]$ and $Na_2[UO_2(P_2O_7)]$. Phosphate ion, like sulfate, prevents the quantitative extraction of uranium with ether from strong nitrate solutions.^{40,41}

Many of the inorganic complexes are of limited interest with regard to the analytical chemistry of the uranyl ion, but their existence should be noted and considered in work involving ionic species, for example, in spectrophotometry and in solvent extractions. In such cases equilibria between simple and complex ions may be important.

(b) Organic Complexes of Uranium(VI). Literally hundreds of organic complexes of uranium salts are known; survey reports have been made.⁴²⁻⁴⁶ Among the important uses of these complexes are colorimetric determinations of uranium, prevention of precipitation, and extraction from aqueous solution.

(1) Complexes of Aliphatic Acids. Acetate ion forms a complex with the uranyl ion in which three acetate groups are bound to one uranyl ion; the complex is anionic. The complex is not stable at low pH presumably because hydrogen ion is more firmly bound to acetate than is uranyl ion.⁴⁷ Other aliphatic acids (formic, butyric, etc.) form similar complexes of the type $[UO_2(O_2CR)_3]^-$, where R is an aliphatic radical.

Oxalate ion also forms a uranyl complex sufficiently stable to prevent precipitation of the rare-earth oxalates. In order to precipitate lanthanum oxalate from solutions that contain a uranyl salt, it is necessary to add sufficient oxalate to complex all the uranium before the lanthanum oxalate begins to precipitate.⁴⁸

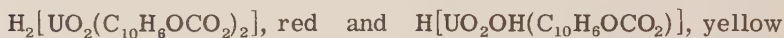
Tartrate, citrate, and malate ions also form complexes that are stable at a high pH. The uranyl tartrate complex contains one molecule of tartrate per uranium atom, as does the malate complex. Both complexes are anionic, and examples of salts^{49,50} are $K[UO_2OH(C_4H_4O_6)]$ and $Na[UO_2OH(C_4H_4O_5)] \cdot 2H_2O$. Both citrate and tartrate ions prevent precipitation of ammonium diuranate by ammonia. The citrate complex is important in uranium-poisoning therapy.

(2) Complexes of Aromatic Acids. Benzoate ion, like acetate, forms a complex anion of the type $[UO_2(C_6H_5CO_2)_3]^-$, of which the ammonium salt is known in the crystalline form. The hydroxybenzoic acids, especially salicylic acid, form numerous complexes, which have been

rather carefully studied. Salicylic acid forms two series of complexes, a yellow series and a red series that contain, respectively, two and three molecules of salicylic acid per atom of uranium. The complexes exist in solution or may be precipitated as insoluble pyridine, aniline, piperidine, and other salts.⁵¹ Aniline salts of the disalicylate series and the trisalicylate series have been made. The salicylate complexes find use in analytical procedures as colorimetric reagents or as agents to prevent the precipitation of uranium with the rare-earth oxalates.^{52,53}

Both *p*-hydroxy and *m*-hydroxybenzoic acids form complexes containing three molecules of acid per atom of uranium; aniline, pyridine, and other salts are known.⁵⁰ Cresotinic acid (2-hydroxy-3-methylbenzoic acid) forms an orange-red complex used in colorimetric analysis.⁵⁴

With *o*-hydroxynaphthoic acid, complexes of this type are formed.⁵⁵



Protocatechuic acid (3,4-dihydroxybenzoic acid) forms complexes of which the guanidine salts have been made. Excess sodium hydroxide is reported to cause no precipitation of uranium from these complexes. Complexes with gallic acid (3,4,5-trihydroxybenzoic acid) are also alkali-stable, and strongly colored, and they may be used for the colorimetric estimation of the uranyl ion.^{56,57} The complex with sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) is also colored and is useful in colorimetric determinations.⁵⁸

(3) Other Organic Complexes. Aromatic polyhydroxy compounds such as catechol and pyrogallol also form colored complexes with the uranyl ion.^{59,60} Some are orange-yellow in color, and a few are red or violet.

Uranyl salts form complexes with disubstituted dithiocarbamic acid, $\text{RR}'\text{NCSSH}$, which are soluble in benzene and other nonpolar solvents.^{420a} The diethyl derivative is extracted with benzene in the analysis of uranium in thorium.⁶¹ The ethyl phenyl derivative acts in the same manner. Both complexes are readily formed at pH 2.8 or 3.0.

Many other extractable uranyl complexes are known. These include the chelate complexes formed with isatin- β -oxime, quinaldic acid, 8-hydroxyquinoline, 1-nitroso-2-naphthol, and antipyrine. These compounds are insoluble in water and generally insoluble in very weakly acidic or basic solution, but they dissolve readily in such solvents as chloroform, methyl isobutyl ketone, and amyl alcohol. Such complexes are essentially neutral molecules, as contrasted with the soluble ionic type complex formed by the hydroxy acids. Complexes of 1,3-diketones with uranyl salts are also known.^{62,63}

(c) Inorganic Complexes of Uranium(IV). The uranium(IV) ion also forms many complexes, among them complexes of the halide, sulfate, sulfite, carbonate, and phosphate ion.

Of the halide complexes, $[\text{UF}_5]^-$ and $[\text{UOF}_3]^-$ are known in the form of potassium and ammonium salts, and $[\text{UCl}_6]^{--}$ is known in the form of sodium and lithium salts. Complex sulfate ions are $[\text{U}(\text{SO}_4)_4]^{-4}$ and $[\text{U}(\text{SO}_4)_3]^{--}$. The sulfite complexes include two well-characterized compounds, $(\text{NH}_4)_4[\text{U}(\text{SO}_3)_4]$ and $\text{Na}_6[\text{U}_2(\text{SO}_3)_7] \cdot 20\text{H}_2\text{O}$. The former resembles the oxalate as well as the sulfate complexes.⁶⁴ Phosphate complexes include salts^{65,66} of the ion $[\text{U}(\text{PO}_4)_2]^{--}$.

(d) Organic Complexes of Uranium(IV). The uranium(IV) ion forms complexes with many of the same organic compounds that also combine with the uranyl ion. Oxalate, for example, forms a stable, soluble complex of the type $(\text{NH}_4)_4\text{U}(\text{C}_2\text{O}_4)_4$ in neutral solutions. Acidification causes uranium(IV) oxalate to precipitate, and the addition of ammonium hydroxide results in precipitation of uranium(IV) hydroxide or the hydrated oxide. An acetate complex of the uranium(IV) ion may also exist, since uranium(IV) oxalate is soluble in solutions of ammonium acetate. However, the solution of uranium(IV) oxalate in ammonium acetate may occur simply because ammonium acetate buffers the solution to about pH 7, at which pH uranium(IV) oxalate is soluble.

Among the salts formed by the carbonate complexes are those with guanidine.⁶⁴

The hydroxy acids such as tartaric, malic, quinic, citric, lactic, and glycolic form complexes with the uranium(IV) ion.^{67,68} Some of these, such as citric acid, prevent precipitation of uranium when the solution is made basic with ammonium hydroxide. The polyhydric phenols such as catechol also form alkali-stable uranous compounds.^{64,69} The complex ion, of which ammonium, potassium, guanidinium, pyridinium, and other salts are known, is $[\text{U}_2(\text{C}_6\text{H}_4\text{O}_2)_7]^{-6}$ or $[\text{U}(\text{C}_6\text{H}_4\text{O}_2)\text{OH}]^-$. The first complex ion may also be regarded as a dimer of the ion $[\text{U}(\text{C}_6\text{H}_4\text{O}_2)_3]^{--}$ after a seventh molecule of pyrocatechol is added.

Uranium(IV) salicylate is slightly soluble in water and readily soluble in organic solvents, as is uranium(IV) acetylacetonate. Other uranium(IV) complexes of the diketones are known, including those of propionylacetone, dibutyrylmethane, benzoylacetone, and furoylacetone.^{62,63} Currently these compounds have limited analytical applications. Highly colored complexes of disalicylal ethylenediamine and its derivatives are known and may have value in analytical work.⁷⁰

Uranium(IV) cupferrate, insoluble in water, is soluble in ether and other organic solvents and is an important complex in the chemistry of the uranium(IV) ion.

2. METHODS OF SEPARATION

2.1 Introduction. The particular method of separation of uranium chosen for a given operation will depend upon such factors as the separation desired, the amount of uranium present, the nature and amounts of the accompanying elements, the accuracy necessary, and the effect of the reagents employed in the subsequent steps of the analysis. It is therefore impossible to evaluate categorically the various methods, but a description of the procedures will be helpful in deciding on the best procedure for the analysis under consideration. Résumés⁷¹⁻⁷³ of general methods of separation have been made.

Precipitation of ammonium diuranate with ammonium hydroxide is one of the most commonly used methods. Its principal limitation is the lack of separation from most of the heavy metals. Since the material is very gelatinous it is somewhat difficult to wash, especially when more than half a gram of uranium is present. Precipitation with pyridine or hexamethylenetetramine is useful for certain separations since these reagents do not absorb carbon dioxide as does ammonium hydroxide.

Removal of most of the uranium from solutions by precipitation of peruranic acid, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, results in the separation from most elements. The precipitate is inclined to be a bit waxy, however, and offers some difficulty in washing when the operation is carried out on a 20- to 50-g scale. A further limitation is that only about 99 per cent of the uranium is removed in a single treatment.

From mildly acid solutions sodium uranyl acetate can be precipitated in a crystalline and easily filtered form. Some excellent separations can be made, but not all the uranium is removed. The sodium magnesium uranyl acetate separation may also be used for separating most of the uranium from solutions.

Precipitation of uranium(IV) oxalate is another method of separating uranium from a large number of other substances; it may be carried out in acid solution. The precipitate is crystalline and filters rapidly. The main objection to its use is that a reduction step is necessary.

The precipitation of uranium(IV) with cupferron is a very useful step in many analyses, and the material may be extracted as well as filtered. The above five precipitation methods [ammonium diuranate, peruranic acid, sodium uranyl acetate, uranium(IV) oxalate, and uranium(IV) cupferrate] constitute the most important and most common procedures, but there are numerous others that have special uses and are particularly adapted to certain types of analytical work.

Precipitation as uranium(IV) iodate is useful for uranium(IV) solutions that contain no other interfering quadrivalent cations; this brings

about separation from uranium(VI). Removal as uranium tetrafluoride is similar but is usually limited to milligram amounts because of the gelatinous nature of the precipitate. Uranium(IV) hypophosphate and pyrophosphate have similar uses, but, being crystalline, they are more suited to analytical use; they may be chosen when the uranium is to be separated but not weighed. Removal as uranyl phosphate is mostly limited to solutions containing no other metals, but by the use of arsenates excellent precipitations and some separations can be made. The principal advantage of precipitation as uranyl sulfide, or as the hexamethylenetetramine uranyl sulfide complex, is that large amounts can be readily filtered and washed. Precipitation with ferrocyanide has little quantitative use. Electrolytic separation as U_3O_8 is rarely used. Trace amounts of uranium may be carried on ferric, aluminum, or calcium hydroxide, barium carbonate, or copper ferrocyanide.

Of the organic reagents cupferron, as already mentioned, is very useful when reduction to the uranium(IV) state is feasible, whereas precipitation with benzenearsonic acid may find a limited use in separations from elements that are not quadrivalent. A number of other reagents are available for precipitation of uranium(VI). Each has its special uses. Thus tannic acid precipitates uranium from carbonate solutions, and oxine separates uranium as a compound that may be weighed, titrated, or extracted by a solvent. Quinaldic acid, isatin- β -oxime, and 1-nitroso-2-naphthol form a precipitate that separates uranium from miscellaneous elements. Those compounds may be extracted as well as filtered.

One of the most useful complexes formed by uranyl salts is that with carbonates. Other reagents that have more specialized applications in complexing uranyl salts are hydroxylamine, citrates, and tartrates. One of the most common uranium(IV) complexes is with oxalates; citrates and tartrates form complexes over a wider pH range.

Extraction procedures in general give particularly clean-cut separations. With micro amounts extractions are usually more quantitative than precipitations. Ether extraction of uranyl nitrate is the most general procedure, and the extraction of various complexes finds special applications. These include chloroform or ether extraction of uranium(IV) cupferrate, aniline extraction of uranyl tannate, and chloroform extraction of uranyl complexes with antipyrine, oxine, etc.

2.2 Precipitation. The addition of a precipitant for uranium to a solution that contains numerous kinds of anions and cations yields in most instances a group separation of uranium along with other elements. If the precipitations can be made in acidic solutions, such

as in the precipitation of uranium peroxide or uranium(IV) oxalate, the separation may be a fairly selective one. Certain nonselective processes are, however, extremely useful, for example, the collection of traces of uranium by coprecipitation with a carrier such as ferric or aluminum hydroxide. If the objective is the gravimetric estimation of uranium, it is in general necessary to use a combination of methods of separation such as removal of acid-insoluble and hydrogen sulfide groups, extractions, mercury-cathode electrolysis, etc., prior to the precipitation of the uranium.

Trivalent uranium, as is well known, is readily oxidized in solution to uranium(IV) either by the oxygen of the air or by hydrogen ion. If a salt of uranium(V) is dissolved in water a rapid disproportionation to a mixture of uranium(IV) and uranium(VI) occurs. Hence uranium(IV) and uranium(VI) are the forms in which uranium is normally encountered. It is necessary to maintain reducing conditions by excluding air or by adding a suitable reducing agent when uranium(IV) is being precipitated as the cupferrate, the oxalate, etc. If an oxidizing attack has been used the uranium will occur in the uranium(VI) state.

The formation of a soluble carbonate complex has long been used for the separation of iron, aluminum, etc., from uranium.²⁷ At ordinary dilutions 1.15 g of ammonium carbonate prevents precipitation of 1 g of uranium(VI). When the ammonium hydroxide precipitate is large, repeated precipitations are necessary. The combined filtrates are then acidified, boiled to remove the carbon dioxide, and treated with ammonium hydroxide to precipitate the uranium. Certain rare earths, particularly members of the yttrium group, are somewhat soluble in ammonium hydroxide-ammonium carbonate solution.

(a) Ammonium Hydroxide Precipitations from Uranyl Solutions. Ammonium hydroxide precipitates uranium completely from uranyl solutions provided complexing ions such as carbonate, citrate, tartrate, and fluoride are absent.^{74,75} This process serves only to separate uranium from many anions and from the alkali metals, the alkaline earths, and the cations that form ammonia complexes, e.g., copper(II), nickel(II), zinc(II), and others. The latter separations require repeated precipitations and are effective only when the ratio of uranium to the other ions is favorable. Under certain conditions the precipitates will carry more or less completely the anions of phosphorus, vanadium, silicon, and boron.

A great number of elements are precipitated in whole or in part by ammonium hydroxide under the same conditions as uranium; these are listed by Lundell and Hoffman.⁷⁶ It is therefore obvious that the ammonium hydroxide precipitation method for the determination of

uranium may be applied only to solutions that are free from interfering elements.

Ammonium hydroxide precipitation may be used advantageously to collect microgram to milligram amounts of uranium by coprecipitation with ferric or aluminum hydroxide. This method of separation is usually followed by other methods such as electrolysis or ether extraction.

Procedure. Since carbonate impurities dissolved in ammonium hydroxide prevent complete precipitation of uranium, the reagent should be fresh. It is well to make a test for carbonate with barium or calcium hydroxide. Ammonium hydroxide solution may be purified from carbonates by distillation, and the gaseous ammonia that is evolved is dissolved in water under an atmosphere of nitrogen. It may also be conveniently prepared from a tank of liquefied NH_3 . If the ammonium diuranate is to be ignited to U_3O_8 for quantitative determination, the ammonium hydroxide should be filtered before use because after standing in glass it always contains suspended siliceous material.

To the uranyl solution that is low in fluorides and free of carbonates, tartrates, and other strongly complexing substances, a few drops of methyl red solution are added. Strongly acidic solutions are nearly neutralized with ammonium hydroxide with stirring. Chloride or sulfate solutions that contain uranium(IV) may be oxidized with a little nitric acid. To the weakly acidic solution is added 5 to 10 g of ammonium nitrate or chloride per 100 ml of solution. Addition of macerated filter paper is advisable. The solution is boiled and NH_4OH (1 to 4) is slowly added with stirring until the solution smells of ammonia. The solution is filtered, and the precipitate washed with hot 2 per cent ammonium nitrate or chloride made basic with ammonium hydroxide.

(b) Pyridine. Pyridine precipitates uranium from uranyl solutions and offers certain advantages over ammonium hydroxide.⁷⁷ Since it is a weaker base it does not absorb carbon dioxide, and the resulting absence of carbonates reduces the danger of incomplete precipitation and precipitation of alkaline-earth carbonates. Large quantities of sulfate interfere. Ammonium nitrate should be present.

Separations are brought about from the alkaline earths, the alkali metals, manganese, cobalt, and nickel, but certain other metals are precipitated by the reagent, including zirconium, titanium, iron, chromium, and aluminum.^{78,79}

Procedure. To the solution that contains 5 to 10 g of ammonium nitrate methyl red indicator is added. Pyridine (20 per cent) is added with stirring until the solution is neutral to the indicator, and then about 10 ml more is added. The solution is heated, and more pyridine

is added if the solution becomes acid to the indicator. The precipitate is filtered and washed with 3 per cent ammonium nitrate containing a little pyridine.

(c) Hexamethylenetetramine. Solutions of uranyl salts that contain ammonium ion and no excess acid precipitate ammonium diuranate⁸⁰ when boiled with hexamethylenetetramine. This reagent is a weak base, and like pyridine it does not absorb carbon dioxide.

Besides uranium, iron, aluminum, ceric ion, zirconium, thorium, and titanium are precipitated, but quantitative separations are made from bivalent ions such as zinc, cobalt, manganese, nickel, and magnesium.

Procedure.⁸⁰ Ammonium hydroxide (1 to 4) is added to the solution just to the point of precipitation. The precipitate is dissolved with a few drops of HCl (1 to 3), and ammonium chloride is added until the amount present is 10 g per 300 ml of solution. The solution is boiled and 10 per cent hexamethylenetetramine is added dropwise until no further precipitation is noted in the supernatant liquid when more reagent is added. Two or three milliliters more of the reagent is then added, and the precipitate is filtered immediately with the aid of filter pulp and washed with hot 2 per cent ammonium nitrate solution. A double precipitation is sometimes necessary.

(d) Peroxide Precipitation. A good discussion of peroxide precipitation is given in Gmelins Handbuch.⁷² Hydrogen peroxide is an important reagent for separation of uranium from rather complex solutions because the precipitation may be made in acidic solutions of pH 0.5 to 3.5.^{72,81} At the lower pH at least 7 per cent hydrogen peroxide must be present in excess of that necessary to form the compound⁸² $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. When $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ is precipitated the solution becomes more acidic, as shown by the equation



The alkaline earths and potassium^{83,84} and sulfate^{25,85} and fluoride⁸⁶ ions appear to interfere with the completeness of the precipitation. Iron also affects the precipitation owing to the catalysis of the decomposition of the hydrogen peroxide.^{72,87} The interference of iron is largely eliminated by addition of malonic⁸⁷ or lactic acid⁸⁸ to complex the ferric ion. Acetic and lactic acids tend to minimize the interference of ferric and cupric ions during peroxide precipitations.⁸⁹ The peroxide precipitation may be made quantitative by freezing the solution and allowing the frozen mixture to stand 1 hr.²¹⁵ Filtration is carried out with the solution at about 2°C until the iron has been removed.

Separation by peroxide has been used for the removal of the bulk of uranium prior to the determination of traces of other metals (nickel, titanium, etc.) by colorimetric procedures.

Procedure.⁹⁰ About 5 g of the metal or its equivalent of oxide is dissolved in approximately 15 ml of HNO_3 (1 to 1). The filtrate is evaporated to near dryness, the residue is taken up in about 50 ml of water, and 4N NH_4OH is slowly added to the solution, with stirring, to a permanent turbidity. Then 2N HNO_3 is added dropwise until the solution is cleared. Five milliliters of 30 per cent H_2O_2 is added to the solution with stirring, and it is then centrifuged for 5 min at about 1,500 rpm. The supernatant solution is decanted through a filter, and the UO_4 is washed twice with a little water. The solution is centrifuged after each washing, and the washings are passed through the same filter. The paper is finally washed with water.

(e) Ammonium Sulfide and Polysulfide. Uranyl sulfide is precipitated as a brown, amorphous substance by ammonium sulfide or polysulfide from solutions alkaline with ammonium hydroxide. The precipitate is said to contain some ammonium diuranate.⁹¹ It is readily filtered and washed.

The precipitation of uranyl sulfide may follow the hydrogen sulfide separation of other elements. After treatment of the acid solution with hydrogen sulfide to remove lead, bismuth, copper, molybdenum, and other elements, the solution may be made basic with ammonium hydroxide, and more hydrogen sulfide passed in. This precipitates iron, zinc, aluminum, and other metals along with the uranium. At this point advantage is taken of the solubility of uranyl sulfide in ammonium carbonate, and efficient separations are thus possible since few other elements behave similarly.

Carbonates, pyrophosphates, citrates, and other ions that complex uranyl compounds prevent the precipitation of uranyl sulfide.

Procedure.⁹¹ About 3 g of ammonium chloride is added to the solution containing not more than 0.25 g of uranium per 150 ml of solution. The solution is heated to about 80°C on the steam bath, made alkaline with ammonium hydroxide, and an excess of either ammonium sulfide or polysulfide is added, or hydrogen sulfide is bubbled into the solution. The solution is filtered, and the precipitate is washed with 2 per cent ammonium chloride that has been made alkaline with ammonium hydroxide.

(f) Hydrogen Sulfide and Hexamethylenetetramine. The uranyl ion is precipitated quantitatively from nearly neutral uranyl solutions containing hexamethylenetetramine when treated with hydrogen sulfide. The composition of the red substance that is precipitated is uncertain.⁹² This treatment may be preferred over uranyl sulfide

since the precipitate formed is crystalline, is readily filtered, and is characterized by negligible adsorption of foreign ions. Good separations from the alkali and alkaline-earth metals are reported.

Procedure.⁹² The uranyl solution is made nearly neutral with NH_4OH and heated to 60°C . Two grams of hexamethylenetetramine is added, and hydrogen sulfide is bubbled in for 15 min. The flask is heated on the hot plate, and the hydrogen sulfide treatment is continued for an additional 15 to 20 min with frequent shaking. After settling for 15 min the precipitate is filtered off and washed with 3 per cent ammonium nitrate made basic with ammonium hydroxide.

(g) Fluorides. Uranium(IV) is precipitated by hydrofluoric acid and yields a hydrated uranium tetrafluoride. Uranium(VI) is not precipitated. As ordinarily precipitated from aqueous mediums, hydrated uranium tetrafluoride is gelatinous and is not easily filtered. Centrifugation is usually preferred.

When precipitated by ammonium or alkali fluorides, uranium tetrafluoride invariably contains much of the accompanying cation as a double salt. Separations are, however, possible from iron and vanadium.⁹³ Removal of small amounts of uranium from large amounts of metals such as zirconium or tantalum complexed by fluorides is probably the most useful application of the fluoride precipitation; even here multiple precipitations may be required. In general, separation of uranium with fluoride should be avoided when possible.

Procedure. To the uranium(IV) solution in a platinum dish is added an excess of 48 per cent hydrofluoric acid. The mixture is stirred with a platinum or plastic rod and allowed to settle, then a drop or two more of hydrofluoric acid is added to the supernatant liquid to determine whether the precipitation is complete. Enough hydrofluoric acid must be added to complex all the iron, zirconium, boron, aluminum, or other such ions. The suspension is warmed, poured into a plastic test tube with rinsing, and centrifuged. The precipitate is washed several times with 2 to 4 per cent HF. Filtration through paper using a rubber or plastic funnel is also feasible.

(h) Iodates. Uranium(IV) iodate precipitated from acid solution serves to separate uranium(IV) from many elements. Uranium(VI) is not precipitated and separation is not made from thorium, titanium, zirconium, or cerium(IV).

Procedure.⁹⁴ The uranium(IV) solution is made 4 to 5 per cent in H_2SO_4 , and an equal volume of hot 10 per cent potassium iodate (in 10 per cent H_2SO_4) is added. The solution is diluted to twice its volume with 0.8 per cent potassium iodate (in 2 per cent H_2SO_4), heated and stirred, cooled a little, filtered, and the precipitate washed with hot 0.8 per cent potassium iodate (in 2 per cent H_2SO_4).

(i) Phosphate. Uranyl solutions treated with a phosphate readily precipitate a uranyl phosphate if the pH is not too low.⁹⁵ With phosphoric acid UO_2HPO_4 precipitates, whereas with diammonium phosphate $\text{UO}_2\text{NH}_4\text{PO}_4$ precipitates. Both of these precipitates are soluble in excess phosphoric or other strong acid. The precipitate formed in absence of ammonium salts is fine and passes through filter paper, but it becomes crystalline upon the proper treatment. The optimum pH for the precipitation is 1.7; the pH should be at least in the range 1.2 to 2.3, which can be obtained by the use of acetic or formic acid. Many elements such as zirconium, thorium, and bismuth are precipitated under the same conditions. The method has been used in ore analysis for the separation from vanadium.

Procedure.⁹⁶ To the solution from which the hydrogen sulfide and the ammonium carbonate-ammonium hydroxide groups have been removed is added about 5 g of ammonium phosphate. The solution is carefully acidified with 30 ml of sulfuric acid (1 to 1) and boiled to expel carbon dioxide. The uranium is precipitated as the phosphate by adding a slight excess of NH_4OH (1 to 1) to the boiling solution (400 to 450 ml volume), followed by a slight excess of acetic acid. The solution is cooled in ice water for about 30 to 45 min and filtered using a filter pump. The precipitate is washed with a solution containing 2 per cent ammonium sulfate made slightly acidic with acetic acid. When only a small amount of vanadium is present one phosphate separation suffices; otherwise a second precipitation is necessary.

(j) Hypophosphate and Pyrophosphate. Hypophosphate and pyrophosphate form soluble complexes with uranyl salts³⁷⁻³⁹ and form insoluble salts with uranium(IV) solutions.^{65,66} In general these two ions precipitate quadrivalent metals from acid solution; examples are titanium, zirconium, thorium, and uranium(IV) salts. Free hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$, or its disodium salt, and sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, may be used.

Precipitated from acid solution, uranium(IV) hypophosphate, UP_2O_6 , and uranium pyrophosphate, UP_2O_7 , are readily filtered. Good separations are made from sexivalent uranium and most trivalent elements. The principal objection to their use is the fact that they introduce phosphorus-containing ions into the solutions.

Procedure.⁶⁵ The uranium(IV) solution, 1N to 3N in sulfuric, perchloric, or hydrochloric acid, is heated to 90 to 100°C, and a 5 per cent solution of hypophosphoric acid, its disodium salt, or sodium pyrophosphate is added with stirring. After the precipitate has settled the supernatant liquid is tested for completeness of the precipitation. The mixture is digested on the steam bath for 30 to 60 min and

filtered, using macerated paper for small quantities. The precipitate is washed with a 1 per cent solution of the precipitating agent containing a little sulfuric acid.

(k) Arsenate. Uranyl salts in weakly acidic solution are quantitatively precipitated by arsenic acid or arsenates as UO_2MAsO_4 , where M is hydrogen, sodium, ammonium, or potassium.⁹⁷ From acetic acid solutions uranyl ammonium arsenate is precipitated as a crystalline, readily filtered compound; excess ammonium salts must be present.

A number of excellent separations may be made by the use of arsenates.⁹⁸ No difficulty results from the presence of small amounts of ferric iron, but in the presence of large amounts prior reduction with sulfur dioxide is necessary to assure separation. Double precipitations are generally required. Satisfactory separations are also made from the rare earths, aluminum, the alkali metals, and the alkaline earths. Cerium should be trivalent. Zirconium, thorium, titanium, silver, and lead interfere.

Procedure.⁹⁸ Excess mineral acid in the uranyl solution is neutralized with ammonium hydroxide, and enough glacial acetic acid is added to make the solution 10 to 20 per cent in this reagent. The uranium concentration should be less than 50 mg per 100 ml at this stage, and the solution should contain 1 g of ammonium chloride or its equivalent per 100 ml. Ammonium salt is added if no neutralization with ammonium hydroxide is necessary. Thirty-five milliliters of arsenic acid (80 g per liter) is added, and the solution is brought to a boil, cooled, and filtered. Standing overnight after precipitation does no harm. The precipitate is washed with dilute ammonium chloride.

When large quantities of ferric iron are reduced with sulfur dioxide, enough acid is formed to prevent complete precipitation of the $\text{UO}_2\text{NH}_4\text{AsO}_4$. This condition is avoided by the buffering action of ammonium acetate, using with every 250 ml of precipitating solution 5 ml of solution containing 20 g of ammonium acetate per 150 ml.

(l) Potassium Ferrocyanide. The well-known reaction of uranyl salts with potassium ferrocyanide, forming a deep-red precipitate or suspension, is not often employed for the quantitative removal of uranium. This limited usage is ascribed to the poor separations obtained as well as the many interferences. To be quantitative the precipitation must be performed in neutral or weakly acidic medium, and the material produced is fine and difficult to wash. When stoichiometric amounts of uranium and ferrocyanide are present the precipitate has the composition $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$, but when excess $\text{K}_4\text{Fe}(\text{CN})_6$ is added some $\text{UO}_2\text{K}_2\text{Fe}(\text{CN})_6$ is formed. Traces of uranium may be carried on copper ferrocyanide and precipitated from acidic solution (pH 0.7 to 1) containing 1 to 2 per cent ammonium nitrate.

One of the few separations possible with ferrocyanide is from beryllium.⁹⁹ Iron, manganese, copper, zinc, and the heavy metals, in general, are completely precipitated. The alkaline earths, alkali metals, and most light metals are completely or partially carried down. Carbonates prevent the complete precipitation of the uranium.

Procedure.⁹⁹ The pH of the solution is adjusted to between 3 and 6 with ammonium hydroxide and acetic acid. The uranium concentration should be less than 1.0 mg per milliliter. Two grams of ammonium chloride is added, the solution is warmed, and 0.3 g of potassium ferrocyanide in a little water is stirred in. The slimy precipitate is filtered with the aid of filter pulp and washed with dilute potassium ferrocyanide.

(m) Alkali Metals. Precipitation of uranyl solutions with sodium hydroxide, under closely controlled conditions, yields a precipitate stated¹⁰⁰ to be $\text{U}(\text{OH})_6$. No analysis of the precipitate is given. Increasing proportions of sodium or potassium diuranate, which are insoluble even in the presence of carbonates, are formed under more strongly alkaline conditions. When uranyl solutions are treated with sodium hydroxide a basic salt is the first substance to precipitate, and it is successively transformed into the hydroxide, $\text{UO}_2(\text{OH})_2$. Thus, from uranyl chloride such basic salts, or mixtures of salts, as $\text{UO}_2(\text{OH})_{1.1}\text{Cl}_{0.9}$ and $\text{UO}_2(\text{OH})_{1.4}\text{Cl}_{0.6}$ may be precipitated.^{100,101} The substances precipitated by strong alkalis are not easily filtered.¹⁰²

Strong alkalis have been used to recover uranium from such materials as uranyl phosphate, which is decomposed into sodium diuranate if caustic soda is used, and trisodium phosphate.¹⁰³ The sodium hydroxide should be at least 9N, and the precipitate may be separated by decanting, centrifuging, or filtering through glass cloth or sintered glass.

(n) Cyanides. Uranyl solutions with the alkali cyanides precipitate a yellow substance¹⁰⁴ that is probably uranic acid.

(o) Triple Acetate Separation. Most of the uranyl ion in a solution may be removed by saturating the solution with sodium nitrate at pH 2.5 and 2.5M in acetate ion. The method is not useful for recovery of traces of uranium, and not more than 0.1 to 0.2 per cent impurities can be present in the solution.⁴⁵⁸

(p) Mercuric Oxide. When boiled with an aqueous suspension of mercuric oxide that contains ammonium chloride, uranyl solutions react, presumably precipitating ammonium diuranate and forming slightly ionized mercuric chloride. Hydroxy acids interfere. Separations are made from the alkali metals and the alkaline earths.

(q) Basic Zinc Carbonate. A suspension of basic zinc carbonate added to uranyl nitrate solution causes quantitative precipitation. The

reaction is hastened by boiling the solution. Iron, aluminum, thorium, and other metals also precipitate.¹⁰⁵

(r) Barium Carbonate. In absence of ammonium salts a suspension of barium carbonate precipitates the uranium from uranyl nitrate as a double carbonate,²⁹ $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$.

(s) Vanadates. Ammonium uranyl vanadate is precipitated when solutions containing uranyl salts and an excess of ammonium metavanadate are buffered with ammonium acetate.

(t) Oxalic Acid. Oxalic acid precipitates quadrivalent uranium as the dioxalate. Certain anions and organic compounds such as fluorides and lactic acid interfere by complexing the uranium ion. Sulfates and large amounts of phosphates should be absent. In a solution previously reduced either electrolytically in a mercury-cathode cell or by zinc amalgam, no cations in moderate amounts interfere with the exception of thorium and the rare earths.

Precipitation should take place in a hydrochloric acid solution. Acidities up to 3N in hydrochloric acid are permissible.¹⁰⁶⁻¹⁰⁸ If the concentration of hydrochloric acid is lower than 2N, other oxalates may precipitate [zinc, iron(II), copper, etc.]. The solubility varies from 5 mg per liter in 0.12N HCl to 500 mg per liter in 6N HCl. If the precipitate is filtered immediately, from 0.5 to 1 per cent of the uranium passes into the filtrate.

Traces of Fe, Ni, and Mn are carried down but no Cr, Cu, or PO_4^{3-} . There is a poor separation from Cb and the rare earths and none at all from Th. The $\text{U}(\text{C}_2\text{O}_4)_2$ may be redissolved in $\text{HNO}_3 + \text{H}_2\text{O}_2$, concentrated H_2SO_4 , or NaOCl at pH 9 to 10.

Procedure.¹⁰⁹ The reduced solution (reduced electrolytically or with 3 per cent liquid zinc amalgam until the red color of trivalent uranium is formed) is filtered into 2 to 6 g of oxalic acid through acid-resistant paper such as Whatman No. 52. If 1 g of uranium is present, if the volume exceeds 250 ml, or if the iron and chromium content is expected to exceed 2 g, then at least 4 g of oxalic acid is used. The reductor and the paper are washed with 3N HCl and 4 ml of stannous chloride solution, 120 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 ml of 6N HCl, is added through the filter paper. The solution is stirred for at least an hour at room temperature. The precipitate is filtered on Whatman No. 42 paper and washed ten times with 10-ml portions of 1 per cent oxalic acid in 3N HCl.

(u) Cupferron. Ions of the following metals are precipitated by cupferron from strong acid solution: iron, gallium, zirconium, columbium, tin, antimony, hafnium, titanium, vanadium, tantalum, and uranium(IV). Among others the following elements are not precipitated: aluminum, chromium, beryllium, phosphorus, manganese, nickel,

zinc, uranium(VI), boron (borate or fluoborate), the alkaline earths, and the alkali metals. The cupferron separation has been used chiefly as a means of separating interfering elements from uranyl solutions before volumetric analysis. Precipitation of the uranium(IV)^{111,112} has been used by several laboratories.

Nitric acid should be absent in cupferron separations, and if precipitates are to be ignited, perchloric acid should also be absent. Sulfuric acid solutions are suitable. Hydrochloric and organic acids can also be used. The two valence states of uranium make possible the double cupferron procedure in which iron, titanium, and others are precipitated from uranyl solutions, and after reduction uranium is precipitated from remaining elements. It has been found necessary to have a reducing agent present in order to ensure complete precipitation. Both hydroxylamine¹¹³ and sodium hyposulfite¹¹⁴ have been used for this purpose. After the second step the uranium(IV) cupferrate, $U(C_6H_5N_2O_2)_4$, may be either filtered or extracted with an organic solvent. The precipitate is flocculent and fairly easily washed.

Procedure.¹¹³ The acidity of the solution is adjusted to 5 per cent H_2SO_4 by volume, 5 g of hydroxylamine hydrochloride is added, and the solution is cooled for 10 min in an ice bath. A 6 per cent cupferron solution is added slowly with stirring until precipitation is complete. Vigorous stirring is continued for 2 min, an additional 5 ml of cupferron solution is added, and the mixture is stirred vigorously for a second 2 min. The precipitate is allowed to stand in the ice bath for another 5 min, then filtered with suction and thoroughly washed with a freshly prepared cupferron wash solution. (Two solutions are prepared, kept cool in an ice bath, and mixed prior to use. The first is 100 ml of a 7.5 per cent volume H_2SO_4 solution; the second is a 50-ml solution containing 0.8 g of cupferron and 3 g of hydroxylamine hydrochloride.) The precipitate is dried at 70°C and slowly ignited until the organic matter has burned off, after which it is heated to 1000°C.

(v) Tannic Acid. Uranyl salts in buffered acetate solution react with tannic acid (digallic acid) to yield a deep-brown voluminous precipitate. The precipitation is quantitative. Carbonates and tartrates cause no interference.¹¹⁷ This method ranks with the ammonium diuranate method in usefulness. Tannin, the glucose ester of tannic acid, also precipitates uranium from hot solutions. Oxalates prevent the precipitation of uranium by tannic acid in slightly acid solution.¹¹⁸

The following elements are precipitated by tannic acid, or tannin, and are listed in the order of decreasing ease of precipitation: tantalum, titanium, columbium, vanadium, iron, zirconium, hafnium, thorium, uranium, and aluminum.¹¹⁸ It is impracticable to separate

adjacent members of this series with tannic acid, at least without the aid of complexing agents such as oxalates or carbonates. Tannic acid separations of uranium from vanadium are also unsatisfactory.¹¹⁹ The alkali metals are not carried down.

Procedure.¹¹⁷ To the uranyl solution, usually containing less than 200 mg of uranium, is added ammonium hydroxide until most of the mineral acid is neutralized. Any excess ammonium hydroxide is neutralized with acetic acid. Smaller quantities of strong acids may be converted to acetic acid by addition of ammonium acetate. After weakly acidic conditions are obtained, 2 ml of 2 per cent tannic acid is added for each 12 mg of uranium. The mixture is heated to boiling, and an ammoniacal 10 per cent ammonium acetate solution is added until the precipitate settles and the upper part of the liquid is clear. The very voluminous, chocolate-brown precipitate is filtered and washed with slightly ammoniacal 2 per cent ammonium nitrate solution. Washing by decantation prior to filtration is desirable when separation from large quantities of other elements, e.g., alkali metals, is being made.

(w) Hydroxyquinoline. Under basic or weakly acidic conditions, 8-hydroxyquinoline precipitates sexivalent uranium quantitatively as a reddish-orange compound. The uranyl 8-hydroxyquinolate forms an addition compound with an extra mole of reagent, precipitating^{120,121} as $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$. The pH range for complete precipitation has been given as 4.1 (reference 122) to 13.5 (reference 123). The compound is easily filtered and extracted and may be titrated with bromine. Uranium(IV) is also precipitated by oxine.

Uranium may be separated from phosphates with oxine, if the phosphates are not present in large amounts, by performing the precipitation at a high pH (10 to 12) and by using an excess of the reagent.¹²³ Small amounts of fluorides, oxalates, lactates, and hydroxylamine do not interfere. Uranyl 8-hydroxyquinolate is precipitated from tartrate-complexed solutions^{124,125} but is dissolved by ammonium carbonate. Advantage is taken of the latter factor in separating aluminum from uranium.¹²⁶ It is necessary to keep in mind, of course, that under the conditions under which oxine precipitates uranium, many other elements, including copper, aluminum, zinc, and thorium, are precipitated.

Procedure (Weakly Acidic Conditions).^{120,121} The acetate-acetic acid buffered solution (pH 5 to 6) of uranyl chloride, sulfate, or nitrate, but not perchlorate if the compound is to be ignited, which is free from interfering ions and contains less than 100 mg of uranium per 100 ml of solution, is treated with an oxine solution (2.5 g of oxine in 5 ml of glacial acetic acid diluted to 100 ml) with stirring until an

excess of the reagent is known to be present. At least 2.5 ml should be used per milligram of uranium. The mixture is heated to 60°C, digested for 15 to 20 min, and filtered. The precipitate is washed with 2 per cent ammonium nitrate solution made slightly ammoniacal.

Procedure (Basic Conditions).¹²³ The uranium concentration and reagent solution described above are satisfactory. The uranyl solution is made nearly neutral with NH_4OH , and the precipitate that forms is just redissolved with dilute sulfuric acid. To the cold solution 10 g of ammonium chloride, nitrate, or sulfate is added. The oxine solution is then added. Ammonium hydroxide, 6N, is added until the solution is just basic. Then 20 ml of silica-free NH_4OH is added, and the mixture is digested at 60 to 65°C for half an hour. If the supernatant solution appears turbid after standing for 15 min, more ammonium salt is added. The mixture is filtered hot, and the precipitate is washed as in the above procedure.

(x) Quinaldic Acid. A number of metals, including uranium, are precipitated by quinaldic acid (quinaldinic acid, 2-quinolinecarboxylic acid, $\text{C}_9\text{H}_6\text{NCOOH}$).¹²⁷ Precipitations with this reagent are generally comparable to those with 8-hydroxyquinoline. The reaction is carried out in the presence of ammonium chloride.

Procedure.¹²⁷ The uranyl solution is prepared for precipitation in the same way as for oxine. The pH should be between 6 and 7, and 5 to 7 g of ammonium chloride should be present per 150 ml of solution. To the boiling solution is added an excess of the reagent, 3.5 per cent sodium quinaldate in water, and after cooling the mixture is filtered on a sintered-glass crucible. The precipitate is washed with 5 per cent hexamine and 5 per cent NH_4NO_3 until free of chloride.

(y) Isatin- β -Oxime. Isatin- β -oxime (β -isatoxime, $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$) precipitates uranium from acetate-buffered solutions as a yellow or yellow-orange substance. The compound carries down some precipitant by adsorption.

This reagent quantitatively precipitates uranium from its tartrate complex, and makes possible separations from cobalt, nickel, and other elements. Modifications yield separations from manganese, zinc, and the alkaline earths.

Procedure (from Tartrate Solution).¹²⁸ To the solution containing 0.002 to 0.1 g of uranium is added 10 ml of 10 per cent sodium acetate made acid to phenolphthalein, 5 to 15 ml of a 2 per cent NH_4CNS solution, 2 to 15 ml of 2 per cent sodium potassium tartrate solution, and 6 to 30 ml of 1 per cent isatin- β -oxime in 50 per cent $\text{C}_2\text{H}_5\text{OH}$. After the precipitate has settled for 15 min it is filtered and washed with 100 ml of a 0.05 per cent isatin- β -oxime solution.

From ordinary acetate-buffered solutions, however, silver, lead, iron, cobalt, nickel, and mercury as well as uranium are precipitated, but thallium, the alkaline earths, and alkali metals are not carried down.¹²⁹

Procedure (from Acetate Solution).¹²⁹ Any mineral acid in the solution to be treated is neutralized with ammonium hydroxide, and the solution is made acid with acetic acid. The solution of 100 ml may contain up to 300 mg of uranium. The solution is boiled, and an excess of the reagent, 1 per cent in 50 per cent alcohol, is added. The solution is removed from the hot plate, and 5 to 15 ml of 10 per cent ammonium or sodium acetate made acid to phenolphthalein with acetic acid is added. The mixture is stirred, cooled, allowed to stand 3 hr at room temperature, and filtered. The precipitate is washed with dilute isatin- β -oxime prepared by diluting 25 ml of the 1 per cent solution to 500 ml.

(z) 1-Nitroso-2-naphthol. Sexivalent uranium is precipitated from weakly acidic or weakly basic solution by 1-nitroso-2-naphthol. The yellow-orange precipitate is very fine. A suitable pH range¹³⁰ for precipitation is 4.0 to 9.4. The compound may be extracted by amyl alcohol.¹³¹

Cobalt, iron, silver, and several other elements precipitate under the same conditions, but zinc, aluminum, the alkaline earths, and the alkali metals do not.¹³¹

Procedure. The uranyl solution is made alkaline with ammonium hydroxide, and the precipitate is dissolved using the minimum amount of nitric acid. A drop or two of ammonium hydroxide is added, and then excess 1-nitroso-2-naphthol solution, 10 per cent in alcohol, is added. One gram of the reagent is used for each gram of uranium. The precipitate is filtered off and washed with water saturated with the reagent.

(aa) Benzeneearsonic Acid. Benzeneearsonic acid [phenylarsonic acid, $C_6H_5AsO(OH)_2$] is more or less specific in that it forms precipitates with ions of quadrivalent metals from solutions of various acidities. Uranium(IV) benzeneearsonate precipitates as a fine, very light-green compound, whereas uranyl salts are not affected. Various derivatives of benzeneearsonic acid may also be useful. These include the *m*-nitro-*p*-hydroxy, *p*-*n*-butyl, and *p*-dimethyl-aminobenzeneazo derivatives.¹³²

Uranium(IV) is quantitatively precipitated by benzeneearsonic acid in weakly acidic solution. Thorium, zirconium,¹³³ hafnium, tin(IV), columbium, and tantalum are also quantitatively precipitated.¹³⁴ Zirconiumbenzeneearsonate also precipitates quantitatively from strongly acidic solutions. Titanium and cerium(IV) are partially precipitated.

Procedure. The acidity of the uranium(IV) solution, free of thorium, zirconium, the earth acids, and other interfering ions, is adjusted with ammonium hydroxide and sulfuric acid until the pH is 1 to 3. The solution is heated nearly to boiling and a 2.5 per cent solution of benzenearsonic acid or its sodium salt is added in excess. The precipitate is filtered off and washed with 0.01N to 0.1N hydrochloric acid.

(bb) **Miscellaneous Organic Reagents.** Uranium(IV) salts resemble thorium salts in that they are precipitated by *m*-nitrobenzoic acid or sebacic acid. Uranium(IV) salicylate is also insoluble.¹³⁵

Under the proper pH conditions, uranyl salts are precipitated by a number of other organic reagents. Both sodium alizarinsulfonate and aluminon give colored precipitates.¹³⁶ A yellow precipitate is formed by boiling with thiosinamine (allylthiourea,¹³⁷ $C_3H_5NHCSNH_2$). Ammonium benzoate and cinnamate have been used to facilitate precipitation¹³⁸ of uranium. 1-Hydroxyadridine¹³⁹ forms a precipitate with uranyl salts similar to that with oxine, but it is soluble in buffered acetate solution. 3,5-Dibromosalicylaldoxime yields a brown precipitate.¹⁴⁰ From acetate-buffered solutions, uranyl salts are thrown down by isonitroso-N-phenyl-3-methylpyrazolone as a reddish-orange substance.¹⁴¹ Some uranyl salts of substituted arsonic acids are difficultly soluble.¹⁴² These include the *p*-aminobenzene-, the 3-nitro-4-hydroxybenzene-, and the methane-arsonic acids. Between pH limits of 1.0 and 4.0, uranium(VI) is quantitatively precipitated by arsanilic acid.¹⁴² Ethylenediamine precipitates a yellow crystalline substance which is redissolved by an excess of the reagent.¹⁴³ A dark-yellow precipitate soluble in acetic acid is formed with diphenylthiocarbazide.¹⁴⁴ Disalicylaethylenediimine and related compounds complex and precipitate uranyl and uranous salts,¹³⁵ but they also form derivatives with most other heavy metals.

Aluminum, beryllium, and a number of other metals are precipitated as their hydroxides in a filtrable form when their solutions are boiled with urea. Uranyl solutions, however, are only partly precipitated as ammonium diuranate; evidently the carbon dioxide formed upon hydrolysis of the urea complexes a portion of the uranium. The dithiocarbamates, $(R_2NCSS)^-$, precipitate or complex many metals, and some of the higher dialkyl compounds, e.g., the di-*n*-butyl derivative, yield water-insoluble, ligroin-soluble uranyl salts.¹⁴⁵ They are decomposed by acids and are of little importance. The substituted xanthates behave similarly.¹⁴⁶

2.3 Carriers. Gathering agents have been used in analytical chemistry for many years to collect a small amount of a precipitate distributed through a considerable volume of liquid.¹³²

For example, hydrous manganese dioxide has been used to gather ferric hydroxide,¹⁴⁷ and microgram quantities of copper have been collected by the addition of a few milligrams of lead and precipitation of both as sulfide.¹⁴⁸

In general, an ion is more completely carried the greater the insolubility of the compound on which the ion is being carried, the greater the insolubility of the compound formed between the ion itself and the precipitating agent, and the greater the similarity in size and chemical behavior of the carrying and carried ions. The more nearly two ions are alike the more apt they are to form isomorphous compounds, and in turn the more likely they are to coprecipitate.

Carriers were used to isolate traces of uranium prior to determination. The carriers for uranium that have been used to the greatest extent for analytical purposes are ferric hydroxide,¹⁴⁹⁻¹⁵³ aluminum hydroxide (see references 150, 151, 154, and 155), calcium hydroxide,¹⁵⁶⁻¹⁵⁹ magnesium oxide,¹⁶⁰ and thorium peroxide.¹⁶¹ Other carriers that have been used for the separation of uranium are barium carbonate¹⁶² and calcium fluoride.¹⁶³

(a) Ferric Hydroxide. Ferric hydroxide has been used as a carrying agent for uranium in the analysis of effluents.^{153,163} In general 2 to 10 mg of iron (0.005 per cent by weight) was added as ferric chloride, followed by an ammonium hydroxide precipitation. The iron residue obtained could then be examined by spectrographic fluorescence or colorimetric methods. In one investigation¹⁶³ it was found that the concentration of uranium left behind after precipitation did not exceed 1 or 2 parts per 100 million parts of solution, which roughly represented the limit of experimental error. The presence of substantial amounts of carbon dioxide, up to 0.01 per cent by weight, did not alter the results measurably.

(b) Aluminum Hydroxide. In a few instances aluminum hydroxide^{150,154,155} has been used as a carrier for trace amounts of uranium chiefly where the presence of iron was not desirable. The reactions are comparable to those obtained with iron. Using 5 mg of aluminum as carrier¹⁵⁵ and ammonium hydroxide as precipitant, it was found that the uranium content of the filtrate was 0.5 to 2.0 γ per 100 ml of solution. Without the aluminum as carrier the filtrate contained approximately 50 γ of uranium per 100 ml of solution.

(c) Calcium Hydroxide. Calcium hydroxide, or lime, has been used both as a precipitant and gathering agent for the isolation of traces of uranium (see references 156, 157, 159, and 164) from solution. It has proved very useful in the presence of carbonate ion^{159,164} with less than 3 γ of uranium per liter left in solution. Calcium has been used

as a collecting agent in alkaline solution to separate traces of uranium from vanadium. The following procedure has been used for the analysis of red sodium vanadate.

Procedure.¹⁵⁶ To a 10.00-g sample in a 600-ml beaker enough water is added to make a slurry. To this slurry is added 30 ml of 50 per cent sodium hydroxide, 300 ml of water, and a few glass beads. The mixture is then covered with a watch glass and boiled vigorously until the volume is about 150 ml. The sample is again diluted with 300 ml of water, heated to boiling, and removed from the hot plate. Ten milliliters of calcium nitrate solution [1.2 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per 100 ml] is added. The solution is allowed to stand until the precipitate settles and is then filtered through a Whatman No. 42 filter paper.

2.4 Complexes. Uranyl ion is precipitated by ammonium hydroxide along with iron, aluminum, and other members of the ammonium hydroxide group.¹⁶⁵ However, in the presence of alkali carbonates it forms complex carbonates that are soluble. In the presence of carbonate, ammonium sulfide does not precipitate uranyl sulfide. Ammonium carbonate inhibits the precipitation of uranyl ion as phosphate. The precipitation of ammonium uranate is inhibited by ammonium oxalate. Alkaline peroxide has also proved effective for complexing uranium. Tartrate, citrate, and malate ions prevent the precipitation of uranyl sulfide and ammonium uranate. Hydroxylamine has been used to complex the uranium and separate it from iron and thorium, and salicylic acid has been used to complex uranium and separate it from the rare earths.

(a) Ammonium Carbonate Separation. Ammonium carbonate has also been used extensively to complex uranium and separate it from other elements of the ammonium hydroxide group¹⁶⁵ such as iron, titanium, and aluminum. The separation from aluminum is not complete, but for certain purposes it has proved adequate.¹⁶⁵⁻¹⁶⁸

The following procedure is illustrative of the ones used.

Procedure.¹⁶⁷ To the solution is added 6N NH_4OH , with stirring, until a slight precipitate forms, which is redissolved with a few drops of 6N HNO_3 . The sample is then poured into a 250-ml beaker containing enough $(\text{NH}_4)_2\text{CO}_3\text{-NH}_4\text{OH}$ solution [2.5 per cent $(\text{NH}_4)_2\text{CO}_3$ in 3N NH_4OH] to contain 3 to 4 mg of $(\text{NH}_4)_2\text{CO}_3$ per milligram of uranium present. Care is taken to rinse all the sample into the solution. The sample is heated to 90°C, stirred, and allowed to digest for 4 to 5 min. One to four grams of diatomaceous earth is added and the solution is filtered through a sintered-glass filter. The precipitate is washed five times with the $(\text{NH}_4)_2\text{CO}_3\text{-NH}_4\text{OH}$ solution. The precipitate is

used for the iron determination and the filtrate for the determination of uranium.

(b) Sodium Carbonate Separation.^{74, 270} If nickel is present the sodium carbonate method is preferred since it will effectively remove iron, titanium, cobalt, nickel, manganese, zinc, beryllium, and the alkaline earths. If the residue is large it is necessary to dissolve it in acid and reprecipitate with sodium carbonate. Aluminum is not separated.

The procedure below has been used for separations in ore analysis.

Procedure.⁹⁶ After removal of the hydrogen sulfide group, the hydrogen sulfide is removed from the solution by boiling, and the solution is oxidized by adding 10 to 15 ml of 3 per cent hydrogen peroxide. Enough sodium carbonate, about 3 g in excess, is added to a volume of 150 to 175 ml to render the solution definitely alkaline, and the solution is then boiled for 15 min and filtered into an 800-ml beaker. The precipitate is washed with a hot 2 per cent sodium carbonate solution and then washed back into the original beaker. The precipitate is dissolved with 10 ml of sulfuric acid (1 to 1) and the sodium carbonate treatment is repeated as before.

(c) Ammonium Sulfide Separation. Trautmann¹⁶⁹ modified Rose's ammonium carbonate-ammonium sulfide method for the separation of uranium from iron, titanium, cobalt, zinc, and manganese. The procedure below is taken from Schoeller and Powell.

Procedure.¹⁷⁰ The solution, 100 ml, contained in a conical flask is treated with excess ammonium hydroxide, 5 g of ammonium carbonate, and a sufficiency of ammonium sulfide; the flask is corked and set aside overnight. The precipitate is collected and washed with water containing ammonium carbonate and sulfide; if bulky it should be dissolved and the precipitation repeated. The combined filtrate is boiled until the ammonium carbonate is decomposed; it is acidified with hydrochloric acid, and again boiled until free from hydrogen sulfide. The uranium is then precipitated with ammonium hydroxide. The precipitate may contain beryllium, phosphorus, and small quantities of aluminum and zirconium.

The alkaline peroxide method for complexing uranium has proved effective when a high pH is necessary in order to remove interfering elements such as the rare earths.¹⁷¹ Hillebrand and Lundell¹¹⁰ recommended the use of sodium peroxide with sodium carbonate. Lundell and Hoffman⁷⁶ list the numerous elements separated from uranium by this reagent. The method has been used chiefly as a means of separating uranium prior to colorimetric analysis^{172, 173} and for removing most of the uranium prior to a rare-earth determination.¹⁷¹

The tartrate, citrate, and malate complexes prevent precipitation of uranium from solutions of high pH but also complex other elements such as iron and aluminum.

Becker and Jannasch¹⁷⁴ laid much stress on the separation of iron and uranium by hydroxylamine. Hecht and Donau¹⁷⁵ have used this reagent to complex uranium in order to separate aluminum, iron, thorium, and the rare earths from uranium in analysis of pitchblende.

Salicylic acid has been used chiefly for complexing uranium in the course of separating rare-earth elements as hydroxides.⁵³

Other methods, whereby complexes of uranium are formed and separated in solution, are considered in Sec. 3 of this chapter.

2.5 Solvent Extractions. The solubility of uranium nitrate in ether has been used for many years for the separation of uranium from many elements.^{176, 177} Hecht and Grunwald¹⁷⁸ used ammonium nitrate as a salting out agent to effect complete separation of uranium in the analysis of ores. Furman et al.^{179, 180} have investigated the effects of salting out and inhibiting agents.

Uranyl thiocyanate complex¹⁸¹ is soluble in organic solvents and uranium(IV) cupferrate is soluble in chloroform.¹¹² Limited use has been made of these compounds for some separations.

(a) Ether Extractions. Two methods of extractions can be used—continuous extraction and batch extraction. Both these methods are applicable to both high- and low-grade uranium-bearing material. The continuous method of extraction efficiently removes all the uranium over a period of time.

The primary requisite for the continuous extraction, as well as the batch extraction, is complete conversion of the original sample to its nitrate prior to extraction.

Several types of continuous extractor, based on the Friedrich continuous extractor for liquids, have been used. Figure 1.1 shows the apparatus used at the National Bureau of Standards, which is similar to the one described by Heberling.¹⁷⁹ The side arm permits addition of nitric acid during the course of the extraction. Several types of extractors have been used at the University of California,^{182, 183} a simple type of which is shown in Fig. 1.2. For rapid extraction of solutions the extractor in Fig. 1.3 has proved useful.¹⁸⁴ The volume used for extraction is only 15 ml, and the time of extraction is shortened to 15 min. For the determination of traces of uranium this volume may be too small and other extractors may be more applicable.

The following procedure is representative of the general ether-extraction methods. Slight modifications are employed, depending upon the specific nature of the sample.

Procedure (Continuous Extraction).¹⁸⁵ One to five grams of dried material is weighed and placed in a 250-ml beaker, the sides of which have been wet with a little water. (If organic matter is known to be present, it should be destroyed by igniting the sample.) To this, 20 ml of HNO_3 is added, and the solution is heated to boiling and digested at

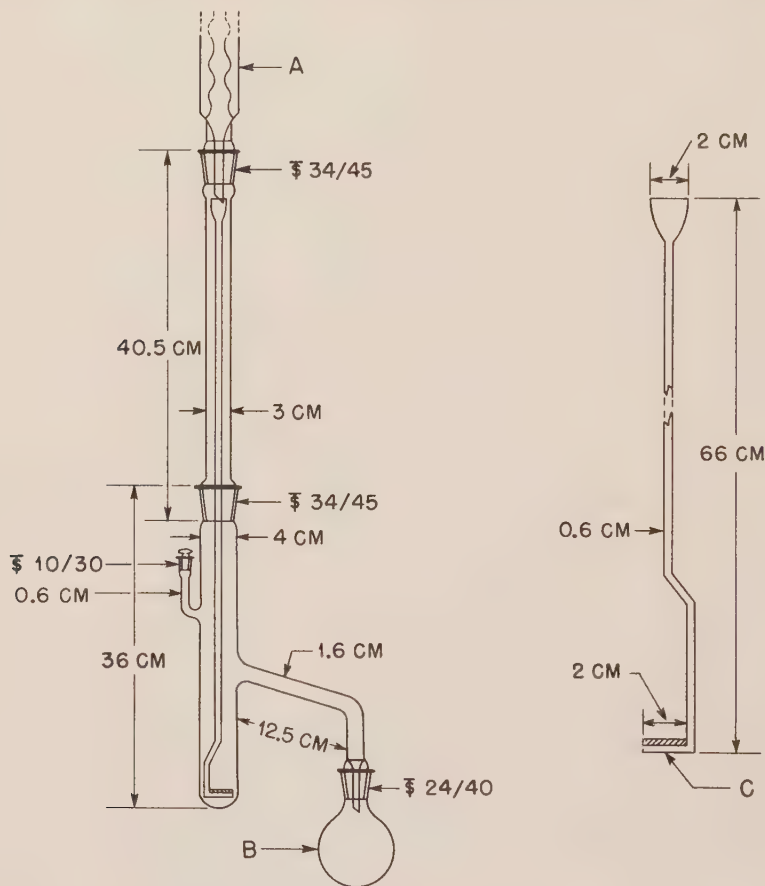


Fig. 1.1 — Continuous extractor. A, condenser; B, 300-ml flask; C, coarse frit.

the boiling temperature for about 30 min. The solution is then filtered, the residue is washed well with HNO_3 (1 to 200), and the filtrate is evaporated to 10 to 15 ml. Any reducing matter is destroyed by adding 0.2 per cent potassium permanganate solution while the evaporation is in progress. No excess of KMnO_4 or MnO_2 should be present just prior to the extraction. If MnO_2 should separate it may be brought

into solution by adding a little sodium nitrite. If phosphate is known to be present its effect is minimized by the use of an excess of ferric nitrate in the extraction. If an appreciable amount of iron is thereby extracted, it may be removed by the use of a continuous multiple extraction. If the unknown sample is a liquid material the sample is

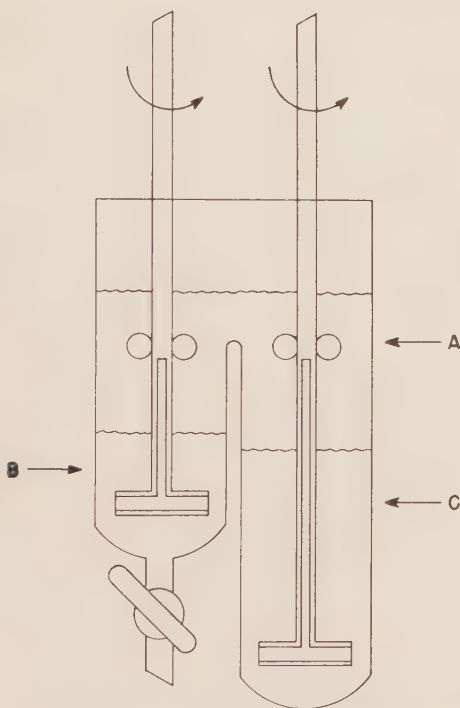


Fig. 1.2—Continuous extractor used at the University of California Radiation Laboratory. A, ether layer; B, solution giving a low distribution of uranium in ether; C, uranyl nitrate solution containing a salting-out agent.

converted to the nitrate, usually by repeated evaporations with nitric acid, and is similarly concentrated to a small volume.

The solution is cooled and transferred to a continuous extractor with the aid of an ammonium nitrate solution (700 g of ammonium nitrate per liter of 10 per cent nitric acid), and extracted with diethyl ether for 30 min. At this time, or sooner if the solution tends to hydrolyze, 10 ml of ammonium nitrate–nitric acid solution (mixture of 5 ml of saturated NH_4NO_3 solution and 5 ml of HNO_3) is added. The aqueous phase is then stirred, and the extraction is continued for another 30 min.

The uranyl nitrate is now in the receiving flask, which was originally charged with 60 ml of water and about 75 ml of ether. The ether is removed after the extraction by evaporation on a steam bath or hot-water bath, and the solution is transferred to a 250-ml beaker. To this is added 8 ml of H_2SO_4 (1 to 1), and the solution is fumed twice to remove HNO_3 . From this point a colorimetric or volumetric

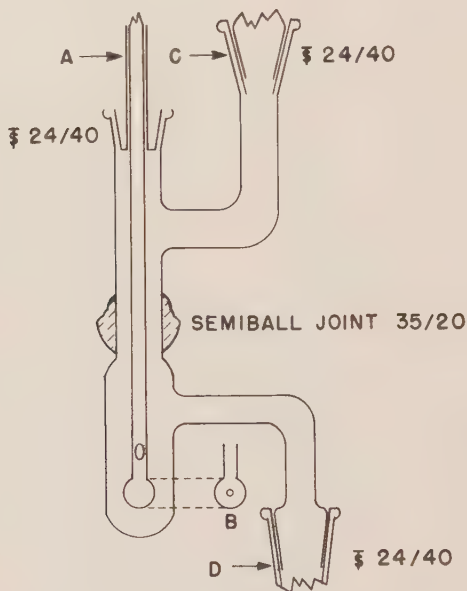


Fig. 1.3—Centrifugal-type semimicro ethyl ether extractor. A, stirrer shaft, close-fitting, powered by variable-speed 110-volt sparkproof motor; B, side view of stirrer; C, joint carrying pyrex, Friedrich's condenser; D, joint, carrying 100-ml flat-bottom flask.

determination of the uranium may be made. If a volumetric method is used it may be necessary to make a cupferron-chloroform extraction to separate impurities.

(b) Interferences in the Ether Extraction. It is evident that the ether extract, whether obtained by continuous extraction or otherwise, should lend itself better to volumetric than to gravimetric estimation of the uranium because other elements are extracted to some extent. With a nitric acid attack no serious amount of antimony or tin remains in solution, and therefore, from the standpoint of oxidation-reduction methods, the chief possible interfering elements are iron, molybdenum, vanadium, and arsenic. Arsenic is not titrated by ceric

sulfate under the conditions used unless a catalyst such as iodide or osmium tetroxide is purposely added. The interference of molybdenum is serious in the extraction only if it occurs as phosphomolybdic acid, silicomolybdic acid, etc. The addition of ammonium nitrate before filtration in the preparation of the original solution helps to remove this interference by precipitation of the ammonium salts of the heteropoly acids. If yellow ammonium salts containing molybdenum appear at the interface during an extraction, it is usually best to repeat the determination by the cupferron-ceric sulfate procedure. The extraction of molybdenum has been found to be almost eliminated by neutralizing most of the excess acid with lime or sodium carbonate prior to extraction.

The only elements that are extracted appreciably with uranium under the conditions used are cerium(IV) and thorium. In a volumetric determination, however, the presence of these elements is of no consequence when ceric sulfate is used in the titration. Ceric ion may be reduced to cerous with sodium nitrite before extraction.

If the amount of vanadium is known to be less than 1 per cent, the error introduced by the amount extracted is not serious. With large amounts of vanadium the error may be minimized by evaporating the nitric acid solution to dryness. There is no effective way known at present of handling with certainty materials high in vanadium, although with materials high in vanadium the uranium may be removed with sodium hydroxide by using calcium hydroxide as a carrier prior to extraction.

Iron, if in high concentration in the aqueous layer, is extracted to a slight extent.

Interfering anions that may tie up the uranium or cause extraction of other elements must be either removed or treated in such a way as to effect complete recovery of the uranium. Fluoride and chloride, for example, should be absent from the nitrate solution because they interfere with the completeness of the extraction of uranium. Chloride causes certain other elements, such as iron(III), to be extracted in the presence of calcium nitrate. Fluoride may be complexed with aluminum nitrate.

Up to 50 mg of sulfate ion in 30 ml of solution does not interfere. Large amounts interfere, but these can be made harmless by adding calcium ion.

Phosphate has been found to decrease the distribution of uranium in the ether-extraction process. Apparently, once the uranium is precipitated as the phosphate no more uranium will be extracted by the ether. It was found that even 12 per cent nitric acid will not redissolve uranyl phosphate. However, the higher the initial concentration

of nitric acid the more uranium will be extracted before precipitation of UO_2HPO_4 occurs. A rather effective method of overcoming the influence of the phosphate ion consists of using ferric or aluminum nitrate, which serves to complex this anion.

(c) Extraction of Uranium Cupferrate.¹¹³ Quadrivalent uranium cupferrate was characterized by Auger¹¹² as soluble in neutral organic solvents. Fryxell and Safranski¹⁸⁶ utilized the treatment of an aqueous

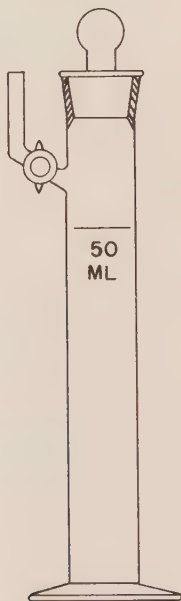


Fig. 1.4—Extraction cylinder.

acid solution of quadrivalent uranium with an organic solution of cupferron for the extraction of uranium to the organic phase. The principle has been utilized for the quantitative separation of milligram amounts of uranium from various elements prior to the colorimetric estimation of uranium with chromotropic acid. This method was later extended to gram quantities.

Extraction or precipitation of quadrivalent uranium cupferrate effects a separation of uranium from aluminum and certain other elements of the ammonium hydroxide group, as well as from the alkali metals, alkaline earths, and several elements of the ammonium sulfide group. Uranium and antimony are the only elements that will survive a double cupferron separation.¹¹³ In the double cupferron separation, an aqueous solution containing the elements in their higher

states of oxidation is treated with cupferron, the precipitated cupferrates are extracted and discarded, and after destruction of the organic matter, the aqueous phase is reduced and extracted with ethereal cupferron. By such a double cupferron procedure, in some cases following certain preliminary separations, uranium can be quantitatively isolated from most uranium-bearing materials.

Procedure.¹¹³ By preliminary separations appropriate to the individual sample a clear aqueous solution of approximately 30 ml is prepared. This solution should be free of organic matter and should contain 0.5 to 5.0 mg of U_3O_8 , 2.5 ml of H_2SO_4 , and negligible amounts of interfering elements. The solution is transferred to an extraction cylinder (Fig. 1.4) using sufficient H_2SO_4 (1 to 200) as a wash solution to bring the total volume to 50 ml. The solution is made uniform, 3 ml of liquid amalgam (see Sec. 3.3b) is added, and the mixture is agitated by vigorous shaking for 5 min. The reduced solution is now extracted with five successive portions of 1.5 ml of ether plus 1.5 ml of ethereal cupferron. (Two grams of cupferron is dissolved in 25 ml of H_2O , the solution is filtered into a small separating funnel, 5 ml of 6N H_2SO_4 is added, and the solution is mixed and extracted with 25 ml of ether.) The mixture in each case is shaken vigorously for 1 min and allowed to stratify for 1 min. The pressure is released by cautiously opening the side-arm stopcock, and the ether layer is then carefully transferred to a platinum crucible by means of a long-stem dropping pipet and evaporated to dryness using an Infra-Radiator.

2.6 Volatilization. Although uranium chloride and uranium hexafluoride can be volatilized, the hexafluoride is the only compound used to any extent for analytical separations.

Because the use of fluorine to remove uranium as UF_6 requires the use of a heterogeneous system, which in this case is a solid reacting with a gas, and also because fluorine is a very reactive gas, it is possible to effect clean separations from those contaminants that do not form volatile fluorides. On the other hand, if compounds of elements such as molybdenum are present, the UF_6 would be expected to be contaminated by the volatile fluorides of these elements. However, even with this complication a clean separation from many common impurities can be effected. Samples containing 75 to 90 per cent uranium oxide, with the remainder as iron, calcium, barium, and aluminum oxides, have been fluorinated successfully with a 99.8 per cent recovery of the uranium.

Larson and Milch¹⁸⁷ showed the effectiveness of the conversion of various compounds of uranium to UF_6 as given in Table 1.1. The apparent incomplete conversion may in some cases be due to insufficient time to complete the reaction since each run was made for only 2 hr.

Table 1.1 — Effectiveness of the Conversion of Uranium Compounds to UF_6

Compound	Conversion, temp., °C	Uranium	
		Found, %	Theory, %
UO_3	450	83.2, 83.6, 82.8	83.2
U_3O_8	500	83.6	84.8
UF_4	500	76.6	76.8
UO_2F_2	350–400	77.4, 79.5	77.3
UO_2	450	90.2	88.2
UC_2	350–400	90.8, 90.8	90.7
$\text{U}_2\text{O}_3\text{P}_2\text{O}_7$	530	67.2, 68.0, 67.8, 66.6	68.2

Fluorinating agents other than fluorine may be employed. Cobalt trifluoride, ceric fluoride, manganic fluoride, or silver difluoride forms UF_6 , which distills out of the reactor¹⁸⁸ when mixed with the oxides, or material from which the uranium is to be separated, and heated to 350 to 400°C. No good quantitative data are available, but with UF_4 recoveries as high as 98 per cent have been noted. Cobalt trifluoride is commercially available.

No volatile uranium compounds are obtained with an anhydrous hydrogen fluoride even at temperatures as high as 700°C. On the other hand, the reaction of anhydrous hydrogen fluoride with many elements and their oxides produces fluorides that are volatile.^{189, 190} Important and typical cases are the reactions of silicon dioxide and tantalum with anhydrous hydrogen fluoride. Both these reactions afford a simple and clean-cut separation of these materials from uranium compounds with which they are associated. Johnston et al.¹⁹¹ report that residues left after hydrofluorination of tantalum–uranium tetrachloride mixtures contained less than 0.05 per cent tantalum, and that the uranium loss was undetectable.

Separation by Hydrofluorination and Fluorination.^{192–194} Mixtures from which uranium can be separated by volatilization procedures are metals and alloys, solids from solutions, and ashes resulting from ignition of residues.

On treating such materials with anhydrous hydrogen fluoride, columbium, tantalum, arsenic, antimony, silicon, tellurium, selenium, etc., are volatilized as fluorides and leave the uranium usually as UF_4 or UO_2F_2 .

Tantalum metal reacts readily with anhydrous hydrogen fluoride whereas Ta_2O_5 is more resistant to attack. Both metal and oxide readily react with fluorine.

Tungsten metal is extremely unreactive to anhydrous hydrogen fluoride, but the oxide WO_3 reacts at a slow rate and gives a residue

of 0.6 per cent of the total after 3 hr of hydrofluorination at 590°C. Both metal and oxide readily react with fluorine. Molybdenum and molybdic oxide react with anhydrous hydrogen fluoride in essentially the same way as tungsten and tungstic oxide.

Vanadium metal, VO , V_2O_4 , and V_2O_5 do not volatilize in anhydrous hydrogen fluoride. The V_2O_5 and VN react but are not completely volatilized after 4 hr. However, the metal, oxides, and nitride are volatile in fluorine.

Titanium oxide slowly reacts with anhydrous hydrogen fluoride, but the volatilization is not complete after 2 hr at 550°C.

Solutions must be treated in such a way as to give a solid residue that contains all the uranium. The solutions may be evaporated to dryness, followed by treatment by the method outlined below, or precipitated with ammonium hydroxide, filtered, and ignited before treatment as described below.

The most important use of volatilization of uranium in analytical methods has been in connection with ignition residues, salvage residues, and refractory solid mixtures in general. From these, separation of uranium by conventional methods is both involved and difficult. The volatilization procedure is simple and is easily carried out.

Procedure.¹⁹²⁻¹⁹⁴ The residues are ground to pass a 30-mesh screen and are treated with nitric acid to make a thick paste and then dried and ignited at 300 to 400°C. This treatment is repeated twice, the lumps being broken up between the ignitions. This breaking up is best done in the nickel boat to be used in subsequent steps. The ignited residue is treated with anhydrous hydrogen fluoride at 700°C until volatile compounds are no longer observed in the exit gas, as evidenced by flame testing. If desired, the exit gas can be scrubbed to recover the volatilized materials.

The residue after the hydrogen fluoride treatment is treated with fluorine at 400°C. Uranium oxyfluoride and uranium tetrafluoride formed in the previous step are converted to UF_6 and quantitatively distilled out into cold traps. (The UF_6 is possibly contaminated by chromium, tantalum, tungsten, molybdenum, or vanadium.) Rare earths, alkaline earths, alkali metals, iron, nickel, cobalt, silver, aluminum, beryllium, manganese, thallium, lead, zinc, copper, mercury, and cadmium remain in the reactor as nonvolatile fluorides.

The method outlined has been used only sporadically, probably because of the aversion of most analytical chemists to using reagents such as hydrogen fluoride and fluorine. Despite this, the use of these reagents makes otherwise difficult separations very easy, and their use should not be overlooked.

2.7 Electrodeposition. The mercury-cathode cell is an analytical tool of great value, which has been used for many years because it allows the disposition of many interfering elements in analytical procedures whereas other elements remain quantitatively in an acidic electrolyte. According to Lundell and Hoffman⁷⁶ the electrolysis of dilute sulfuric acid solutions of the elements results in the quantitative deposition of bismuth, cadmium, chromium, cobalt, copper, gallium, germanium, gold, indium, iridium, iron, mercury, molybdenum, nickel, palladium, platinum, polonium, rhenium, rhodium, silver, thallium, tin, and zinc. Arsenic, lead, osmium, and selenium are quantitatively separated from the solution but are not quantitatively deposited in the cathode. Antimony, manganese, and ruthenium are incompletely separated from the electrolyte. Other elements do not deposit in the mercury cathode from acid solution.

Since uranium does not deposit in the mercury cathode from acid solutions, the mercury-cathode cell affords a convenient and useful means of removing the major impurities from uranium solutions prior to the analytical determination of uranium. Without the danger of loss, this technique allows the separation of uranium from even large amounts of depositable impurities in one operation. Disadvantages, however, include the fact that some more or less common impurities such as aluminum, titanium, and vanadium are not removed from the electrolyte by mercury-cathode electrolysis and the fact that mercury-cathode electrolyses are very time-consuming in cases where large amounts of impurities are to be removed or where the proper electrolytic conditions are not employed.

The effects of various electrolytic variables upon the deposition of chromium, copper, iron, manganese, molybdenum, nickel, and zinc have been determined.¹⁹⁵ In general, average deposition rates increase with increases in current intensity, cathode area, rate of stirring, temperature (up to 25 to 40°C), and concentration of the cation being deposited. Average deposition rates decrease with increase in acidity (copper and zinc are relatively unaffected), electrolyte volume, immersion of the anode, amount of anodic oxygen stirred into the electrolyte, temperature (above 25 to 40°C), impurities in the mercury cathode, and the concentration of uranium in the electrolyte.

In most cases it is difficult to remove the last traces of the cations being deposited. For example, the deposition of the last 10 per cent of the original amount of iron or chromium present in the electrolyte requires approximately as much time as the first 90 per cent. In the presence of 10 g of uranyl sulfate no detectable amount of molybdenum is deposited in the mercury cathode.¹⁹⁶

The order of deposition of chromium, copper, iron, molybdenum, nickel, and zinc from synthetic impure uranium solutions agrees, with the exception of zinc, with that indicated by oxidation-reduction potentials. The deposition order is: zinc-copper, nickel-iron, chromium, and molybdenum. On the average the total time required to deposit all the cations of a given mixture is approximately equal to the sum of the deposition times of those cations when electrolyzed individually.

The optimum conditions for the electrolytic purification of sulfuric acid solutions of uranium with the mercury cathode may be summarized briefly as follows: electrolyte volume, 50 ml; free sulfuric acid concentration, 1N; current density, as high as practicable with the given acid concentration (maximum limit of about 10 amp); anode, a flat platinum spiral or grid just making contact with the surface of the electrolyte; cathode area, as large as practicable; stirring, surface of the mercury cathode is stirred rather rapidly; temperature of electrolyte, between 25 and 40°C (tap-water cooling is usually satisfactory); cathode mercury for the cathode, pure; anions, chloride, nitrate, and phosphate ions should be absent, or present in only small amounts.

Details and reference listings for mercury-cathode electrolysis of uranium-containing solutions are given in the chapter on electrolytic methods.

Electrolytic Removal of Uranium. Uranium may be quantitatively removed from acetate-buffered solutions or the carbonate complex by electrolysis.¹⁹⁷⁻¹⁹⁹ The uranium is deposited on the cathode as an oxide whose chemical and physical nature depends upon conditions. The rate of deposition is much greater at elevated temperatures (80 to 90°C). The yellow trioxide may be deposited at a high pH (approximately 6) when the electrolysis merely lowers the acidity. Reduction occurs in more acid solutions (approximately pH 3), and the uranium deposits as U_3O_8 or UO_2 , or as a mixture, which is black or greenish black.²⁰⁰ At a pH below 4 all the uranium is not removed, but the deposit produced at a pH of 5 is not firm and flakes easily.²⁰¹ A pH of 5 to 7 is recommended, because in the analytical removal of uranium the composition of the oxide formed is immaterial. More details are given in the chapter on electrolytic methods.

Molybdenum is not removed from uranium because it also deposits on the cathode as an oxide.²⁰² Good separations can be made from the alkali and alkaline-earth metals and zinc.^{199, 203}

Procedure. The solution containing a uranyl salt is made basic with ammonia and acidified with acetic acid, or excess ammonium

carbonate is added (ammonium acetate concentration is approximately 0.5M). The pH should be 6 or above. The usual uranium concentration is about 200 mg per 100 ml. A platinum dish serves as the cathode, and a platinum spiral or gauze, preferably rotating, is the anode. The solution is maintained at 80 to 90°C and electrolyzed at 2 to 6 volts with a cathode current density below 0.2 amp/sq cm. The uranium is usually all removed in an hour or two; the electrolysis is continued until a portion of the solution fails to give the ferrocyanide test. The solution is poured out through a filter if necessary, and the oxide remaining is washed with dilute ammonium acetate. Ignition yields weighable U_3O_8 .

3. METHODS OF DETERMINATION

3.1 Introduction. Gravimetric methods for uranium require, in general, the absence of or the prior separation of numerous other elements. They are used chiefly when macro amounts of uranium are available. The normal weighing form is the oxide U_3O_8 . This substance is formed upon proper ignition of any one of the following precipitates—ammonium diuranate, uranous fluoride, uranium dioxide, uranium peroxide, uranous oxalate, uranous cupferrate, and uranyl oxinate. Many other precipitates formed by organic reagents on ignition also give U_3O_8 . Since many of the procedures used for gravimetric determination are also used for separation, Sec. 2 should be consulted.

The electrodeposition of uranium oxide was utilized chiefly in connection with the preparation of samples for isotope ratio determination (see the chapter on electrolytic separations methods).

Titration procedures are generally considered to be the most satisfactory ones for the estimation of macro quantities of uranium. Micro titrations may be performed satisfactorily, but colorimetric methods and other optical or electrical methods are generally preferable for the estimation of small quantities of uranium. Methods based on the prior reduction of uranium to the uranium(IV) state have been utilized most frequently. If uranium(III) is formed during the reduction, aeration serves to convert uranium(III) to uranium(IV) prior to the titration. Any one of the oxidants—potassium permanganate, potassium dichromate, ceric sulfate, ferric chloride, ferric sulfate, and, less commonly, potassium bromate—is used for the titration in the form of a standard solution. The prior separation of iron, vanadium, titanium, and the hydrogen sulfide metals, especially arsenic, antimony, and molybdenum, is generally necessary. Nickel interferes with the

reducing action of the Jones reductor²⁰⁴ but not with other methods of reduction.

Titration of uranyl solutions with strong reductants such as chromous²⁰⁵ or titanous solutions²⁰⁵⁻²⁰⁷ are possible.

The volumetric precipitation of uranyl ion with a standard ammonium phosphate solution has found limited application chiefly for rough assays.²⁰⁸

Colorimetric estimations that are made either visually or with the aid of colorimeters, and especially with photoelectric photometers and spectrophotometers, have been extensively used for the estimation of small percentages of uranium, ranging from about 1 per cent down to a few thousandths of 1 per cent, or in the concentration range of from several hundred to a few micrograms per milliliter. The sodium hydroxide-sodium peroxide colorimetric procedure may be applied in the presence of vanadium, and considerable use has been made of it. The ferrocyanide method is suitable for the concentration range of 8 to 40 γ of uranium per milliliter. Of the many colorimetric methods the most sensitive ones are in general applicable only to uranium solutions that are substantially pure.

Under optimum conditions as little as 10^{-11} g of uranium in a sodium fluoride bead may be detected by the characteristic fluorescence in ultraviolet radiation. The intensity of the fluorescence radiation may be measured with the aid of suitable filters and a photoelectric photometer. The method has been used extensively for various problems involving trace estimations, including biochemical studies. Details regarding apparatus are found in Sec. 3.14 on techniques and in Chap. 24 on "Photometric Methods."

The intensities of the various relatively strong lines in the emission spectrum of uranium are too low to make this method as effective as certain other methods for traces of uranium. The limit of detection under the most favorable conditions is estimated to be 0.1 γ on copper electrodes (see Chap. 26 on "Spectrochemical Methods").

Amounts of uranium ranging from 1 mg down to 1 γ can be estimated polarographically. In general, a considerable amount of prior separation is necessary. The indirect estimation based upon the catalytic uranium nitrate wave is the most sensitive, but it is of little general utility because it requires separation of uranium from the majority of anions and cations (see Chap. 25 on "Electrometric Methods.")

Radioactive counting methods are of primary importance in dealing with material in which the natural ratio of the uranium isotopes has been altered; they are also important in the chemistry of fission products. Counting methods based on the radium content of uranium ores

and minerals have been much utilized, especially where thorium was known to be absent. A discussion of counting methods is given in Chap. 28 on "Radiochemical Analytical Methods."

The mass-spectrographic method has been the only alternative to radioactivity counting methods when questions of isotopic ratios of uranium have been involved. The method has been much utilized for special problems (see Chap. 29 on "Other Methods").

3.2 Gravimetric Methods. Gravimetric determinations of uranium are most frequently completed by ignition of the precipitate to the black or greenish-black oxide U_3O_8 . Other weighing forms have been proposed, for example, UO_2 , which is obtained by heating and cooling in hydrogen.²⁰⁹ Uranyl hydrogen phosphate or uranyl ammonium phosphate yields the pyrophosphate upon ignition.²¹⁰ Uranyl ammonium vanadate has been stated¹¹⁰ to yield $V_2O_5 \cdot 2UO_3$ upon proper ignition. No advantages appear to be associated with the three latter weighing forms. Uranyl oxinate has the composition represented by the formula $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$ after it is dried to constant weight at $130^\circ C$.¹²⁰ See Sec. 2 on the methods of separation for further discussion.

Ammonium diuranate, other uranium oxides, and organic compounds of uranium in general yield the oxide U_3O_8 upon proper ignition. A temperature of 800 to $1050^\circ C$ under good oxidizing conditions should be used. At lower ignition temperatures a product richer in UO_3 than U_3O_8 may be obtained.²¹¹⁻²¹³

Organic compounds of uranium must, in general, be ignited cautiously with gradually increasing temperature and good access of air in order to avoid mechanical loss or volatilization. If organic compounds are covered with oxalic acid prior to the ignition the chances for mechanical and other errors are minimized.

The gravimetric method gives results that agree with results from the volumetric method to within 1 part per thousand.⁷⁵

Platinum crucibles are preferable for the ignition of U_3O_8 . Silica crucibles are very slowly attacked by the oxide at $1000^\circ C$.

Uranyl 8-hydroxyquinolate is the only important organic weighing form for uranium. It is precipitated from acetate-buffered solutions and carries down an extra mole of oxine. After the precipitate is dried at $130^\circ C$ for 2 hr, its composition corresponds to the formula $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$. Errors in this method are less than 0.1 per cent. The material may be weighed or titrated with bromine. When heated to $200^\circ C$ the extra mole of oxine is driven off and the color changes from brick-red to olive-green, but it has not been shown that the product thus formed is a satisfactory weighing form for quantita-

tive analysis. The compound with the higher molecular weight is preferred. Ignition with oxalic acid yields U_3O_8 .

(a) Precipitation with Ammonium Hydroxide. Carbonate-free ammonium hydroxide precipitates ammonium diuranate quantitatively from uranyl solution at a pH of 4 or higher.

Ammonium salts should be present during the precipitation, and the solution must be free from substances that form stable complexes with uranyl ion. The chief complexing agents are carbonate, citrate, tartrate, and fluoride ions, but many organic substances and a few other inorganic ions interfere with complete precipitation.

It is important to use ammonium hydroxide that is free from carbonate or dissolved silica. If qualitative tests for carbonate and nonvolatile matter indicate that the reagent is unsuitable, it is preferable to prepare the reagent from gaseous ammonia and carbon dioxide-free distilled water. Ammonia gas that is passed from a cylinder through a tube charged with lime into distilled water will give an adequate solution.

Procedure.⁷¹ A solution that is free from interfering elements and organic matter of all kinds and is slightly acid with mineral acid, preferably HNO_3 , is prepared. The solution is boiled until it is free from CO_2 ; it is allowed to cool a little, and some paper pulp is added. NH_4OH (1 to 4) that is free from CO_2 is added with stirring until it is present in slight excess. Ammonium hydroxide should be added until the solution smells distinctly ammoniacal. At the change point of methyl red the pH is not sufficiently high. The solution is boiled to coagulate the precipitate, and precautions are taken against bumping. The boiling should be continued at least 5 min, and if necessary a little more ammonium hydroxide should be added. The precipitate has a tendency to peptize and pass through the paper. The precipitate is allowed to settle and, after filter pulp is added, is filtered by decantation through a Whatman No. 40 filter paper. It is then washed with hot 2 per cent NH_4NO_3 solution to which a few drops of NH_4OH has been added. The paper and precipitate are transferred to a tared platinum crucible and dried, and the paper is burned off at 800 to 850°C. The precipitate is weighed as U_3O_8 after it is cooled in a desiccator.

(b) Precipitation with Other Bases. Pyridine⁷⁷ or hexamethylenetetramine⁸⁰ may be used instead of ammonium hydroxide. The procedure is analogous to that with ammonium hydroxide, and the chief advantages are: (1) carbon dioxide interferes less, owing to the lower base constants of pyridine and hexamethylenetetramine; (2) the separation from copper, nickel, zinc, magnesium, and cobalt is more complete than with ammonium hydroxide.

The precipitate that is given by pyridine is said to be $\text{H}_2\text{U}_2\text{O}_7$ and is usually ignited and weighed as U_3O_8 .

The usual interfering elements must be absent; concentrations of ammonium sulfate greater than 10 per cent interfere seriously. In the presence of 15 per cent $(\text{NH}_4)_2\text{SO}_4$ it was necessary to use pure $\text{C}_5\text{H}_5\text{N}$ in considerable excess to arrive at a quantitative precipitation. Separation from the alkaline earths is stated to be particularly good by this method.

Procedure.⁷¹ To the weakly acidic solution, preferably nitric, of the UO_2 salt free from CO_2 , methyl red is added as an indicator, and the solution is heated to boiling. With good stirring a 20 per cent solution of pyridine is slowly added until the $\text{H}_2\text{U}_2\text{O}_7$ is precipitated as a yellow precipitate and the indicator changes color. About 10 ml excess of pyridine solution is added, and the solution is allowed to stand on the water bath until the precipitate coagulates and the solution clears. If the indicator again becomes red, pyridine is added. The precipitate is filtered and washed with hot 3 per cent ammonium nitrate, the paper is burned off, and the precipitate is weighed as U_3O_8 .

(c) Precipitation with Hydrogen Peroxide. Hydrogen peroxide precipitates uranium peroxide from acidic solutions²¹⁴ of pH 0.5 to 3.5. The precipitation is quantitative only under certain conditions of temperature, pH control, excess peroxide, time of standing, and absence of certain foreign ions.⁸³ Quantitative recovery may be had by freezing the solution, allowing it to stand, and then warming to 2°C and filtering.^{215,216} Addition of ammonium hydroxide may be necessary to keep the pH in the desired range.²¹⁷

Peroxide in excess is required for complete precipitation, but no harm results from a large excess; there is no advantage in adding more than a twofold excess.⁸² Sulfate ion interferes with complete precipitation of uranium²⁵ if the sulfate-to-uranium ratio is 1 to 1 or greater. Under proper conditions separations may be made by the peroxide method from sodium,²¹⁸ magnesium,²¹⁹ calcium,²²⁰ aluminum,²²¹ rare earths,²²² titanium,²²³ nickel,²²⁴ lithium, cobalt, manganese, copper, and cadmium.⁸⁴

Alkaline earths, when present in high concentration, and vanadium are adsorbed.

Cations that interfere are those which are adsorbed and those which are precipitated under like conditions, e.g., thorium, zirconium, hafnium, potassium, ammonium, and iron.⁸³ Iron interferes by catalyzing the decomposition of hydrogen peroxide (see references 214, 215, 225-228). The interference of iron may be more or less completely eliminated by complexing the iron with lactic,²²⁹ malonic,²²⁸⁻²³⁰

or acetic acid⁸⁹ or by cooling.²¹⁵ Some iron may precipitate even though it is complexed.²²⁷ Thorium is completely precipitated by hydrogen peroxide. Zirconium and hafnium are also precipitated. Potassium and ammonium ions retard the precipitation.

Certain anions retard or interfere with the precipitation. Chloride retards the precipitation,⁸⁴ and, as has been stated, sulfate and fluoride interfere seriously.^{85, 86}

The washing of the precipitate is important, and a wash solution that contains 3 per cent hydrogen peroxide and ammonium nitrate and has a pH of 2.0 to 2.5 is recommended.²²¹

Procedure. It is desirable to have the sample in nitrate or acetate solution. Chloride ion is permissible although it lowers the rate of precipitation. The pH is adjusted to 2.0 to 2.5 by adding ammonium hydroxide. Iron, if present, is complexed with lactic acid at this point. The solution is cooled almost to freezing, and 30 per cent hydrogen peroxide is added with stirring. Twice the stoichiometric equivalent of hydrogen peroxide assures complete precipitation. The entire solution is frozen at -45°C in a dry ice-alcohol cooling bath and held at this temperature for at least 1 hr. The sample is then thawed, filtered, and washed with a peroxide-nitrate solution, 3 per cent NH_4NO_3 having 3 per cent H_2O_2 and pH 2.0 to 2.5. The temperature of the solution should not exceed 2°C until interfering amounts of iron have been removed. The precipitate may usually be collected on a Whatman No. 42 filter paper that has been previously wet with the wash solution, but if the precipitate is fine and somewhat gummy such as in samples high in iron, a dense sintered-glass filter is needed. In this case the uranium is dissolved and precipitated as ammonium diuranate. The precipitate is ignited and weighed as U_3O_8 .

(d) Precipitation with Phosphate. The phosphate precipitation is useful at times because it obviates separation⁹⁵ from P_2O_5 . The phosphate may be dissolved in dilute sulfuric acid and the uranium reduced and determined volumetrically. Ignition of the phosphate precipitate as a gravimetric procedure has been criticized.⁴⁵⁹

The precipitate produced by alkali phosphates tenaciously retains alkali metals, and gravimetric results are always high. If mono-ammonium phosphate¹⁷⁶ is used, a crystalline precipitate that filters well is produced after boiling for 30 min, and accurate results are obtained.

Procedure.⁷¹ A somewhat acid solution, free from other metals that have insoluble phosphates, is prepared. The hot solution is neutralized to an incipient precipitation with NH_4OH (1 to 1) and cleared with a few drops of HNO_3 ; an excess of 10 per cent ammonium phosphate solution is added. The solution is boiled, and NH_4OH (1 to 1) is added drop by drop until precipitation is complete. The solution is

then boiled for 30 min, allowed to settle, and filtered, and the precipitate is washed with 5 per cent ammonium nitrate solution and ignited to $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

(e) Precipitation with Oxalic Acid. As discussed under methods of separation, oxalic acid precipitates uranium(IV) quantitatively. The solution should be free from organic compounds that complex or precipitate uranium(IV). Fluoride and large concentrations of sulfate or phosphate should not be present. If the solution has been reduced previously by mercury-cathode electrolysis or by zinc amalgam after an ammonium hydroxide precipitation, no cations that are present in moderate amounts interfere except thorium and the rare earths. A solubility correction, which depends on the hydrochloric acid content, is necessary.

Precipitation is made in a hydrochloric acid medium, usually somewhat more concentrated than 3N, with about 6 per cent oxalic acid. When the concentration of hydrochloric acid is lower than 2N other oxalates may precipitate, e.g., zinc, iron(II), and copper. If the precipitate is filtered immediately, from 0.5 to 1 per cent of the uranium passes into the filtrate.²³¹ After the solution is chilled and allowed to stand the precipitation is more nearly quantitative.²³² The procedure is that given under oxalic acid separation in Sec. 2.2. The precipitate is ignited and weighed as U_3O_8 .

(f) Precipitation with Tannin.^{71,170} The tannin complex of uranium is bulky, and hence the use of tannin is more particularly suitable for small quantities of uranium. The tannin complex is soluble in mineral acids and hot acetic acid but insoluble in dilute ammonium hydroxide. It is also insoluble in ammonium carbonate and ammoniacal solutions of such salts as ammonium acetate, oxalate, and tartrate; therefore it is of great value in recovering uranium from solutions after such elements as iron have been precipitated. Since tannin precipitates a very large number of elements from ammoniacal solutions the usual preliminary separations must be made.

Procedure.⁷¹ A solution free from iron, aluminum, chromium, vanadium, columbium, tantalum, titanium, zirconium, hafnium, and thorium is prepared. The subsequent procedure varies slightly according to whether acetates, tartrates, or oxalates are present. If acetates are present the solution is nearly neutralized with NH_4OH and boiled, and 5 g of NH_4Cl , an excess of a fresh 5 per cent tannin solution (at least 5 parts tannin to 1 part of uranium), and a 10 per cent ammoniacal ammonium acetate solution is added until the precipitate flocculates and the liquid clears. The solution is mixed with paper pulp, allowed to stand at least 12 hr, and washed with a slightly ammoniacal ammonium nitrate solution. If the precipitate is large it

is washed back into the beaker, stirred with wash liquor, and again filtered. The precipitate is washed, ignited, and weighed as U_3O_8 .

(g) **Precipitation with 8-Hydroxyquinoline.**⁷¹ Hecht and Reich-Rohrwig¹²⁰ have strongly recommended this procedure, after suitable separations, for the gravimetric determination of small quantities of uranium in minerals, etc.

Procedure.⁷¹ The chloride or nitrate solution is evaporated to a small bulk, neutralized with ammonium hydroxide, and treated with 1 or 2 g of ammonium acetate and enough acetic acid to give a 5 per cent solution. The solution is heated to boiling, and an excess of a solution of the reagent is added drop by drop. (The reagent is prepared by dissolving 3 g of oxine in 3 ml of acetic acid, pouring into 100 ml of hot water, cooling, and filtering.) The solution is cooled, filtered through a sintered-glass crucible, washed with warm water, dried at 105°C, and weighed. The precipitate is stated to have the formula $UO_2(C_9H_6ON)_2C_9H_7ON$ and to contain 33.86 per cent uranium.

The procedure for other gravimetric methods is essentially the same as that given in the section on separation.

3.3 Volumetric Methods. The general volumetric methods of determining uranium are (1) reduction to the quadrivalent state and titration with a standard oxidizing solution, (2) titration of uranyl salts with a precipitating agent such as standard phosphate, ferrocyanide, or alkali, and (3) precipitation of a uranium compound such as the 8-hydroxyquinoline derivative and titration of the precipitating agent carried down. The first method is by far the most common and, in general, the most accurate. The second method is rapid and may be used when approximate results are satisfactory. An attractive feature of the third method is that 12 equivalents of bromine are required to titrate 1 mole of uranium.

If only the uranium(IV) content is desired, in many instances the sample may be dissolved with the aid of ceric sulfate or ferric salts. The ferrous ion that is formed, which is equivalent to the uranium(IV) content, is then titrated in the usual manner. This method is applicable only to certain substances such as UO_2 , U_3O_8 , UF_4 , and UCl_4 .

Although uranyl solutions can be titrated directly with standard titanous or chromous solutions, reductimetric procedures are rarely used owing to the rigid precautions required to preserve the standard reductants. A chromous titration to avoid interference by fluoride has been used.²³³ It is usually easier to prepare quadrivalent uranium and use an oxidimetric titration instead.

The reduction of the uranium is generally accomplished by means of zinc—although occasionally silver, chromous ion, or electrolytic methods are used—and it ordinarily gives a mixture of trivalent and

quadrivalent uranium. Except in some potentiometric titrations the trivalent uranium is air-oxidized to the quadrivalent state. Quantitative reduction directly to the quadrivalent state may be achieved with liquid zinc amalgam or silver under certain controlled conditions. The silver reductor has been used extensively for routine work in some laboratories. However, the reduction must be made at a controlled elevated temperature and the reductor requires frequent regeneration. Amalgamated zinc in the form of a Jones reductor is the most convenient and widely used reductant. However, with liquid zinc amalgam, if fresh amalgam is used for each sample, there is less interference by substances that plate out in the amalgam.

The most common oxidizing agents used for titrating reduced uranium solutions are potassium permanganate, ceric sulfate, potassium dichromate, and ferric sulfate. End points may be detected either by indicators or by electrometric means. A precision better than 1 part in a thousand may be obtained with any one of these oxidants in macro titrations, but with smaller amounts of uranium (< 10 mg) the errors increase. Below approximately 10 mg small reductors and microburets should be used. As little as 0.1 mg of uranium may be determined with errors of ± 2 per cent by titration with dilute ceric sulfate²³⁴⁻²³⁶ or potassium dichromate.²³⁷ By the use of specially designed apparatus and electrometric titration, amounts ranging from 0.2 to 0.4 mg of uranium may be determined with 5 to 10 per cent error even in the presence²³⁸ of iron.

The choice of titrant depends on a number of factors including speed of reaction at room temperature, possible objections to the addition of iron or phosphoric acid as catalysts, facilities for protecting hot solutions from air oxidation, interfering substances, the stability of the titrant, and the accuracy desired. The only titration that proceeds to a satisfactory end point directly at room temperature without the addition of a catalyst is the one with permanganate. With this oxidant chlorides must be absent, however, unless the usual preventive solution of phosphoric acid and manganous sulfate is used. Furthermore, permanganate is not so stable as dichromate or ceric sulfate. Room-temperature titrations carried out with ceric sulfate or dichromate in the presence of excess iron and/or phosphoric acid, or by the addition of an excess of titrant followed by back-titration with ferrous salts are quite satisfactory. The visual end point may be more sensitive in titrations with ceric sulfate than in titrations with dichromate, owing to the chromium color, but if such precision is necessary the dichromate end point may be determined potentiometrically. In precision work, dichromate has the advantage of being a primary standard. Most titrations with ferric solutions must be made at elevated tem-

peratures and therefore must be protected from air oxidation; but since large amounts of iron do not interfere, ferric titrations can be used for samples that contain iron.

Titration with potassium bromate is less accurate, giving errors up to 0.4 per cent, but it may be used in the presence of hydrochloric acid, and the solution is not contaminated with substances such as phosphate or ceric salts that are sometimes undesirable. The oxidation of quadrivalent uranium by excess periodate and a titration of the excess periodate by iodide reduction and thiosulfate titration is feasible but seems to offer no practical advantages.²³⁹

Electrometric titrations permit the accurate determination of the amount of overreduction in various solutions and also the determination of several metals in the same solution, but they are too time-consuming for most routine work. However, the ferric sulfate potentiometric method has been extensively investigated and adopted²⁰⁴ because it eliminates the interference of large amounts of iron. The uranium (IV)/(VI) end point in ferric titrations may also be detected by means of thiocyanate but not so accurately as in the potentiometric procedure. Thiocyanate cannot be used as an internal indicator in ferric chloride titrations unless the temperature is kept below 90°C, because the red ferric thiocyanate end point is destroyed at higher temperatures. Determination of the uranium (III)/(IV) end point by potentiometric titration eliminates the aeration step as well as the removal-of-oxygen step, which is necessary in titrations made at elevated temperatures. The amperometric titration of uranium with a ferric solution may be made at room temperature, but it gives somewhat larger errors than the potentiometric titration.^{241, 242} However, molybdenum apparently does not interfere.

(a) Standards. Standards were prepared for use with volumetric methods and are considered under this section.

Two classes of standard uranium materials have been used: (a) the primary standard U_3O_8 , and (b) standard analyzed samples of ores.

Primary Standards. To serve as a primary standard a substance must meet the following requirements:²⁴³ There must be reasonable ease of preparation and accurate reproducibility; the purity must be determinable with sufficient accuracy; and the purified material must be stable under ordinary conditions of the laboratory. The primary standards arsenious oxide, potassium dichromate, and sodium oxalate have been used. However, the use of a standard uranium material is advantageous because the titration and end point in the standardization are the same as in actual analysis, and the weighing error in a standardization is decreased because of the high equivalent weight of uranium.

Uranium metal cannot be prepared in as pure a state as U_3O_8 and is difficult to sample without oxidizing. It is used, however, in certain gas evolution procedures.

Uranium dioxide has a varying composition and cannot be dried at 110°C without some oxidation.

Uranium trioxide is not satisfactory because of its hygroscopic nature.²⁴⁴

Recrystallized uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, after air-drying is subject to slightly varying hydration, but it may be used, if analyzed, as a secondary standard. When dried at 115°C it becomes anhydrous and is slightly richer in uranium than the formula indicates. Its solutions are unstable, especially in light.²⁴⁵

Uranium(IV) uranate, U_3O_8 , is the only pure uranium material that has been employed as a primary standard. A standard sample of this material, designated as MS-ST, has been widely used.

The standard sample of U_3O_8 , MS-ST, has been analyzed by various laboratories. Spectrographic analysis indicated the absence of any significant amount of impurities. The loss on ignition varied from 0.02 per cent at 800°C to 0.05 per cent at 1100°C , but this loss varied less than 0.01 per cent for any given temperature over a period of 4 months.²⁴⁶ The results of volumetric assays²⁴⁷⁻²⁴⁹ are given in Table 1.2.

Ore Standards. The standard ore samples are homogeneous pitchblende, carnotite-bearing sandstone, and monazite samples, which represent the various grades of uranium ores encountered in analyses and which have been analyzed by a sufficient number of methods and analysts to establish their composition with considerable certainty. These samples are very useful as a check upon analytical procedure in ore analysis, since errors arising from factors such as solubility of precipitates, varying concentrations, and effects of one element upon the precipitation of another affect both sample and standard alike.

(b) Reduction. The most common means of reducing uranyl solutions is by amalgamated zinc^{75,202} usually in the form of a Jones reductor but frequently as the liquid zinc amalgam. The reduction has been made by boiling uranyl solutions with pure zinc.^{202,235,250}

(1) Jones Reductors (Solid Zinc Amalgams). The preparation and use of Jones reductors that contain zinc amalgamated with 1 to 5 per cent mercury have been described elsewhere.^{110,251} A proper reduction by this means always gives a mixture of trivalent and quadrivalent uranium and must be followed by an aeration or other special oxidation step.³¹² The amount of amalgamated zinc used in the reductor varies from about 200 to 800 g. Solutions that contain as much

as 17 mg of uranium per milliliter can be reduced satisfactorily by passing the sample at a rate of 15 ml per minute through 180 g of 2 per cent amalgam in the form of a column 20 cm long. Larger reductors are used for low-grade ore samples in order to eliminate interference of traces of some metals by letting them plate out in the upper part of the reductor. Solutions may be passed through large

Table 1.2—Volumetric Assay of U_3O_8 Designated as MS-ST

Laboratory	Reference	No. of determinations	Standard used	U_3O_8 found, %
National Bureau of Standards	246	14	$K_2Cr_2O_7^*$	99.93 ± 0.01
Princeton	247	12	$K_2Cr_2O_7^*$	99.95 ± 0.01
Princeton	248	11	$As_2O_3^\dagger$	99.95

*National Bureau of Standards standard No. 136.

†National Bureau of Standards standard No. 83.

reductors as fast as 60 ml per minute, but more washing is required than for the small reductor. In routine practice the sample in 100 ml of dilute sulfuric acid (1 to 19) is washed from the reductor with about three 30-ml portions of dilute sulfuric acid (1 to 19) and three 30-ml portions of water. This sometimes leaves 0.1 per cent of the uranium in a 600-g, 40 cm long reductor.²⁴⁹ The washing is more efficient if each wash is allowed to drain to the top of the zinc column before the next wash is added.

It has been stated that traces of hydrogen peroxide are formed when air reacts with the zinc amalgam, but there is no evidence that this occurs with sulfuric acid solutions. Furthermore, hydrogen peroxide is completely destroyed when a sulfuric acid solution of it is passed through a zinc reductor.²⁵²

Sulfate and perchlorate solutions are most commonly used for reduction in the amalgamated zinc in the Jones reductor with subsequent titration. Chlorides are also satisfactory if precautions are taken to prevent interference in the titration. Other anions that cause negligible interference are borate and fluoborate.

Micro quantities of uranium may be reduced in a small Jones reductor containing a column of zinc about 50 mm in length and 7 mm in diameter. A stopcock is avoided by having a sintered-glass disk sealed into the bottom of the tube. The uranyl solution, 2 to 10 ml, is drawn through the reductor with suction; no liquid flows otherwise.²³⁴

Substances other than uranium that are reduced by zinc and subsequently titrated must be absent.⁷⁶ Nitrates and nitrites are partially

reduced to substances such as hydroxylamine, which are oxidized by the titrant. Nitric acid or nitrates are often held tenaciously and cannot be removed completely by washing of precipitates or even by double fuming with sulfuric acid.^{71,111} Acetates in large quantity lead to somewhat high results and are also surprisingly difficult to remove by fuming with sulfuric acid. Polythionic acids, which are sometimes introduced by the prior removal of a metal with hydrogen sulfide, also interfere in the titration. Organic matter, particularly that which is easily oxidized, must be removed. This includes formates, oxalates, tartrates, and alcohol. In order to remove these substances the solution usually is fumed with sulfuric acid in the presence of potassium permanganate, perchloric acid, or ammonium persulfate. Ions such as fluorides, oxalates, and hypophosphates which precipitate uranium(IV) should be absent.²³⁷ The presence of 0.3 to 0.4 g of phosphoric acid per sample of 0.4 to 0.5 g of uranium has little or no effect on the result obtained for uranium (see reference 237). However, if the phosphate content is appreciably greater than this, uranium phosphate precipitates in the Jones reductor and in the reduced solution and gives low values. Phosphate retards the reduction of uranium solutions because samples that contain 0.1 to 0.5 g of phosphoric acid are increasingly difficult to reduce, and those that contain 1.0 g of phosphoric acid are virtually impossible to reduce satisfactorily.

There is no interference from the more electropositive metals such as the alkali metals, including ammonium ion, the alkaline earths, beryllium, aluminum, thorium, and the rare earths with the exception of europium. The latter is reduced in the Jones reductor and might be incompletely oxidized by aeration; the low solubility of europous sulfate might also cause trouble.²⁵³ Zirconium, cobalt, zinc, and manganese are also permissible. Metals that plate out on the zinc and interfere if present in too large quantities include nickel, cadmium, copper, silver, gold, mercury, arsenic, antimony, bismuth, tin, lead, selenium, tellurium, and platinum. Nickel can be tolerated only in amounts less than about 300 mg in a reductor that contains 180 g of zinc amalgamated with approximately 2 per cent mercury by weight.²⁰⁴ The plating out of the nickel is accompanied by excessive evolution of hydrogen and incomplete reduction. However, Grimaldi²⁵⁴ has found that a 10 per cent Jones reductor is not poisoned by nickel-bearing solutions; even after 5 g of nickel had passed through, no nickel was found plated out in the reductor. Either hydrochloric or sulfuric acid solutions may be used. The valence changes during reduction of uranium, iron, vanadium, titanium, and molybdenum are the same for the 10 per cent reductor as for the 2 per cent reductor.

This amalgam is prepared by shaking 180 g of 20-mesh zinc for about 2 min with 400 ml of solution containing 23.6 g of mercuric chloride and 10 ml of nitric acid.

Metals that are reduced by the reductor and that interfere in the titration by consuming the oxidizing agent are iron, tin, molybdenum, vanadium, tungsten, and columbium. Titanium and chromium may also be included in this group, but the aeration step completely oxidizes titanium(III) to titanium(IV) and chromium(II) to chromium(III) unless they are present in excessive amounts.

Preparation. An approximately 2 per cent amalgam is prepared as follows: 180 g of 20-mesh c.p. zinc is cleaned by washing with 100 ml of nitric acid (1 to 200) and rinsing three times with water; then it is activated by washing with sulfuric acid (1 to 19) for about 10 sec; after rapid rinsing with three 100-ml portions of water, it is amalgamated immediately by stirring for 10 min with 100 ml of 3.6 per cent mercuric chloride (23.6 g of mercuric chloride per 400 ml of solution) containing a drop of sulfuric acid. The solution is removed by decantation, and the amalgam is washed several times with sulfuric acid (1 to 100). The reductor tube, about 16 mm in diameter, is filled with water, the amalgam is introduced about an inch at a time, and each portion is gently tamped in place with a glass rod.

Procedure. A new reductor, or one that has been idle, is washed with four or five 30-ml portions of sulfuric acid (1 to 19). Then a clean flask is attached to the reductor, and the sample solution, which contains as much as 17 mg of uranium per milliliter in sulfuric acid (1 to 19), is drawn through the amalgam at a rate of 15 ml per minute. The column is washed with five 30-ml portions of sulfuric acid (1 to 19) and then 30 ml of water. After the first wash the rate of flow is increased to about 30 ml per minute. Each wash is allowed to drain to the top of the amalgam before the next is added. This procedure leaves less than 0.05 mg of uranium in a column 19 mm in diameter and 20 cm in length. The rate of flow and amount of washing used vary with the size of the column, the uranium concentration, and the precision desired.

(2) Liquid Zinc Amalgams. Liquid zinc amalgams reduce uranyl salts to the uranous condition as do the solid amalgams. However, as reported by Nakazono,²⁵⁵ sexivalent uranium may be quantitatively reduced to the quadrivalent form by shaking with a saturated mercury-zinc liquid amalgam in an atmosphere of air. Princeton workers²⁵⁶ recommend shaking the 5 to 15 per cent sulfuric acid solution of uranium with 5 ml of liquid zinc amalgam for 5 min and separating the amalgam as suggested by Nakazono. Other workers²⁵⁷ found that 6 per cent sulfuric acid gave low results but that 10 per cent sulfuric

acid was satisfactory. The interference of nickel and other metals that plate out in the Jones reductor is avoided by using fresh amalgam for each sample; this is practicable owing to the ease of regenerating spent amalgam. Micro quantities of uranium are also quantitatively reduced to the quadrivalent state by liquid zinc amalgam, but the reduction conditions are critical.^{236,258} Using micro technique, reduction in air gave a blank, which was apparently due to hydrogen peroxide and was equivalent to about 5 parts of hydrogen peroxide per million parts of solution;²³⁶ a blank of 8 ppm is obtained on the macro scale.²⁵⁶ The micro reduction blank obtained in air varies as much as 50 per cent, but in a carbon dioxide atmosphere it becomes reproducible and much lower. It may be eliminated entirely if the reduction is followed by a permanganate treatment and then by another reduction, all under carbon dioxide.²³⁶ In determination of 0.1 to 1.0 mg of uranium in the presence of 20 γ of chromium, increasing amounts of chromium appear to have an increasing inhibitory effect on the reduction of uranium to the quadrivalent state by liquid zinc amalgam.²⁵⁸

Preparation. In the preparation of the liquid zinc amalgam²⁵⁶ (2.4 per cent zinc by weight), 50 g of 20-mesh granular zinc, which has been thoroughly washed with sulfuric acid (1 to 50), and 2 kg of mercury are heated overnight under 100 ml of 1N sulfuric acid on a low-temperature sand bath. After cooling, the water layer is discarded and the amalgam is transferred to a separatory funnel. The liquid part is allowed to flow slowly into 1N sulfuric acid under which it is left until needed. The solid part is substituted for granular zinc in a subsequent preparation. Fresh amalgam is used for each determination. The spent amalgam is washed with 20 per cent sulfuric acid and transferred to a separatory funnel; the liquid part is allowed to flow slowly into 20 per cent sulfuric acid, is washed with 1N sulfuric acid, and is amalgamated as above.

Procedure.²⁵⁶ The uranyl solution containing 10 to 15 ml of sulfuric acid and no organic matter is transferred quantitatively to a 250-ml separatory funnel (Fig. 1.5) using sufficient ice-cold wash water to bring the total volume to 100 to 110 ml. Five milliliters of liquid zinc amalgam is added, and the mixture is shaken for 5 min. While the separatory funnel is held in an inverted position, the stopcock is carefully opened in order to release any pressure that may have developed. After returning the funnel to an upright position, its stopper is removed and washed thoroughly; the washings are caught in a 500-ml Erlenmeyer flask. The separatory funnel is provided with a rubber stopper on the stem to fit a 125-ml filter flask; the latter has a rubber atomizer bulb attached to its side arm. After the

addition of 75 ml of 1 per cent sulfuric acid to the filter flask, the flask is closed by inserting the separatory funnel stem and stopper. Pressure is built up in the flask with the aid of the atomizer bulb, then the separatory stopcock is carefully opened, and air is allowed

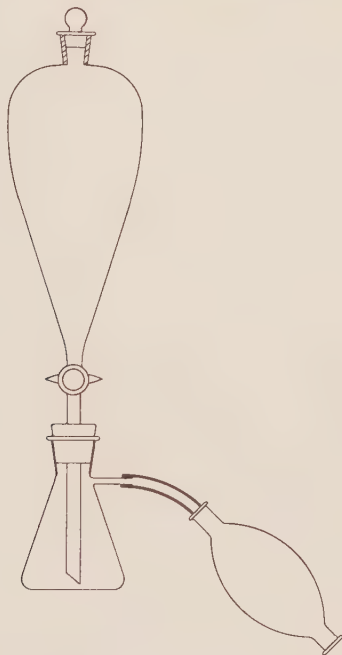


Fig. 1.5—Apparatus for separating reduced solution from liquid amalgam.

to escape. The amalgam flows down, when sufficient air has escaped, while being washed by the ascending dilute sulfuric acid. The stopcock is quickly closed as the last of the amalgam leaves the funnel. If a few drops of amalgam remain in the funnel a little mercury is added, and the resulting dilute amalgam is allowed to flow down, being washed at the same time by ascending wash acid. After the wash solution has been completely pumped up into the funnel, the funnel is separated from the flask, the reduced solution is drained into the 500-ml Erlenmeyer flask, and the funnel is washed thoroughly. The reduced solution is then titrated.

(3) Silver Reductor. Birnbaum and Edmonds²⁵⁹ reported that uranium in hot 4M hydrochloric acid solution is reduced quantitatively to quadrivalent uranium in the Walden silver reductor. The high acidity

raises the uranium (VI)/(IV) potential; the high chloride concentration lowers the Ag/AgCl potential. Beans et al.²⁶⁰ later recommended a slightly modified procedure in which 50 ml of solution, 4M in sulfuric acid and 1M in hydrochloric acid and containing 100 to 400 mg of uranium, was heated to 70 to 90°C and passed through a preheated reductor at a rate of about 20 ml per minute. The reductor was washed with 150 ml of the hot 4M sulfuric acid - 1M hydrochloric acid solution, and the reduced solution was caught in 10 ml of 0.5M ferric alum solution. The uranium was determined directly by titration in the cold with 0.1N ceric sulfate using 1,10-phenanthroline ferrous complex indicator solution in the presence of phosphoric acid. It was also stated that 5 to 50 mg of uranium could be determined precisely provided a smaller reductor and 0.01M ceric solution were used. Best et al.²⁶¹ used a micro silver reductor with 5 mg of uranium and found a decided dependence of the extent of reduction upon the temperature and rate at which the uranyl solution was passed over the silver. The reductor was completely jacketed so that the temperature could be accurately controlled, and the solution was passed through at a fixed low rate. At 50°C reduction to the uranium(IV) stage was 55 per cent complete; at 80°C it was 105 to 110 per cent complete, which indicates overreduction. There is also evidence that dissolved oxygen may be reduced to form traces of hydrogen peroxide during reduction.²⁶²

The silver reductor reduces iron, copper, molybdenum, and vanadium but not titanium or chromium. Acetates do not interfere, but nitrates should be absent. Small amounts of silver chloride dissolve in the strong acid and precipitate after dilution, but this does no harm. Several laboratories have used the silver reductor extensively for control work.²⁶³⁻²⁷² Unless the procedure is carefully controlled the results have a tendency to be low, owing to aging of the silver column or possibly to exposure to air of the hot reduced acidic solutions before titration. In a modification²⁷² to prevent the latter, the reduced solution was chilled by attaching a coil condenser immediately below the hot reductor and leading the solution directly into an excess of oxidizing agent. This procedure required that the sample solution be passed through the reductor at a rate of only 3 to 4 ml per minute. The precision did not appear to be improved.

Preparation.^{264, 273} A sheet of copper weighing at least 30 g is added to a solution containing 100 g of silver nitrate in 1 liter of water and is allowed to stand without stirring for at least 24 hr. Then the remains of the copper plate are removed, the solution is stirred violently to break the precipitated silver, and the supernatant solution is poured off immediately. Water is added to the silver precipi-

tate, the mixture is stirred violently, and the liquid is decanted. The washing and decanting are continued until the wash water contains no suspended silver. The silver precipitate prepared in this manner allows a fast flow of solution through it. The coarse silver is transferred to the reductor, which is equipped with a steam jacket and a

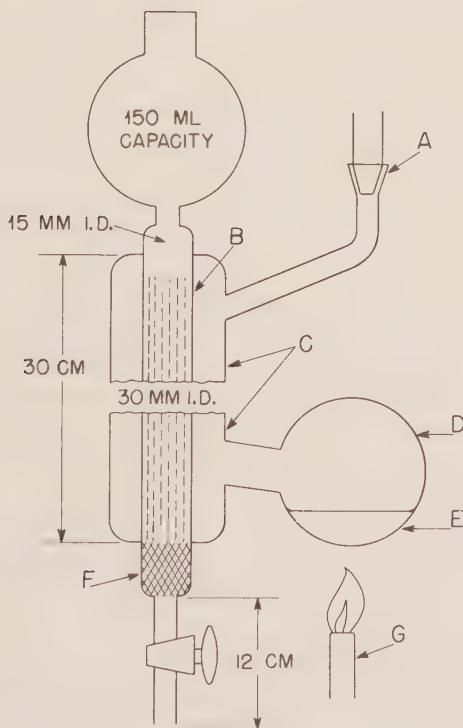


Fig. 1.6 —Silver reductor with steam jacket and boiler (see reference 264). A, reflux condenser connected by rubber stopper or ground-glass joint; B, silver; C, steam jackets; D, 100-ml round-bottom flask; E, water; F, glass wool; G, microburner.

boiler (Fig. 1.6). A column of silver, 12 cm high by 1.5 cm in diameter, is sufficient. It is washed with about 200 ml of Birnbaum solution²⁷⁴ (115 ml of H_2SO_4 and 65 ml of HCl added to 600 ml of H_2O and diluted to 1 liter) and the solution is never allowed to go below the top of the silver column. Water is added to the boiling compartment and heated for 30 min; if any metallic copper is mixed with the silver it dissolves in the Birnbaum solution. The silver is washed again with 150 ml of Birnbaum solution and a blank sample is run.

If not more than 1 drop of 0.1N ceric sulfate is required the reductor is ready for use. Continuous use of the reductor gradually converts the silver to silver chloride, which darkens and serves as an index of the amount of silver available. The silver may be regenerated by rinsing with three 50-ml portions of distilled water, covering with 0.1M sulfuric acid, inserting a zinc rod through the silver chloride until it touches the silver, and leaving overnight or until the color of the column indicates complete reduction. Before being used again the reductor is rinsed and filled with Birnbaum solution. Regeneration may be carried out much faster by means of a chromous chloride solution.^{266,275} About 15 g of crystalline chromic chloride is dissolved in about 50 ml of water in a 250-ml Erlenmeyer flask. Approximately 10 g of granular zinc is added to the flask, and hydrochloric acid is added until there is a rapid evolution of hydrogen. When the solution turns blue it is added to the reductor and allowed to percolate through the silver-silver chloride column. For a time the solution is green as it leaves the reductor. When it comes out blue the reduction is complete. This procedure requires about 30 min.

Procedure.²⁶⁴ A 50-ml aliquot, which contains 100 to 400 mg of uranium and no nitrate or other ions that are reduced by the silver reductor, is placed in a 300-ml flask; 8 ml of hydrochloric acid and 20 ml of sulfuric acid are added. The water in the silver reductor jacket is boiled until refluxing starts. The solution is poured into the reductor, and the flask is rinsed with small portions of Birnbaum solution (see the section on preparation). The solution is allowed to run through the reductor at a rate just under a continuous stream (about 5 min) and is caught in a 500-ml Erlenmeyer flask, which is immersed in ice water containing 10 ml of 1N ferric alum solution. The original flask and the reductor are washed with 150 ml of Birnbaum solution added in six 25-ml portions. Each portion is drained to 1 cm above the silver column before the next is added. The last portion is left in the column. After the addition of 5 to 10 ml of phosphoric acid the solution is titrated directly with 0.1N ceric sulfate using 1,10-phenanthroline ferrous complex indicator.

(4) Chromous Solution.^{276,277} Chromous sulfate may be used for the reduction of uranium to the quadrivalent state prior to potentiometric titration. It lessens the time required for reduction and allows titration in a smaller volume than usual, with a consequent improvement in end points and rate of attainment of potential equilibrium. Cupric, silver, lead, stannous, bismuth(III), mercuric, and antimonous ions are reduced to metallic state by chromous ions, whereas cadmium, ferrous, cobaltous, nickelous, manganous, aluminum, and zinc ions are not. A solution containing 500 mg of uranium and no interfering

ions may be reduced with chromous sulfate and titrated potentiometrically with ferric sulfate with a precision better than ± 0.1 per cent. The chromous solutions may be stored under a carbon dioxide atmosphere or over zinc amalgam. However, the length of time that the chromous sulfate is in contact with zinc amalgam seems to affect the sensitivity of the indicator platinum electrode during the titration; the sensitivity with solutions that had been stored over zinc amalgam for 3, 10, and 21 days was good, poor, and very poor, respectively.

Procedure.^{276,277} A saturated chromous sulfate solution, 5 per cent in sulfuric acid, is prepared by boiling chromic sulfate solutions over liquid zinc amalgam and is stored under a carbon dioxide atmosphere. The sample solution in 5 per cent sulfuric acid is placed in the titration cell and heated to 95°C under carbon dioxide with stirring. The saturated chromous sulfate solution is added until the cell potential becomes more negative than -0.200 volt. The sample is then titrated potentiometrically with ferric sulfate.

(5) Electrolytic Reduction. Although electrolytic reduction usually is not rapid or convenient enough for a routine procedure, it does have the advantages that the reduction may be accomplished simultaneously with electrolytic removal of impurities^{274,278} and that no foreign ions are added. However, special precautions must be taken to avoid interference by peroxide compounds. A mixture of trivalent and quadrivalent uranium is obtained.

(6) Reduction with Lead. Like silver, finely divided lead reduces uranyl chloride to the uranium(IV) salt in hydrochloric acid solutions.²⁷⁹ Liquid lead amalgams act similarly.²⁸⁰ No uranium(III) is formed.

(7) Reduction with Cadmium. Cadmium acts as a milder reducing agent than zinc. Small crystals, prepared electrolytically, were used to pack a reductor; a column 70 mm in height was sufficient.^{281,282} In 3N sulfuric acid, uranyl salts were reduced to uranium(IV), and only traces of uranium(III) were formed. The precautions necessary with zinc reductors were observed. Iron, titanium, molybdenum, vanadium, tin, columbium, chlorates, and others are reduced. For small quantities of uranium, 10 mg, a pointed cadmium rod served to reduce the metal at 100°C in a centrifuge tube.²⁸³

Cadmium amalgams can be prepared in the same fashion as the liquid zinc amalgams and can be used to reduce uranyl solutions in an analogous way, only a little trivalent uranium being formed.²⁸⁴⁻²⁸⁷ An atmosphere of carbon dioxide in the reduction vessel was recommended.

(8) Reduction with Bismuth. Liquid bismuth amalgams can be prepared similarly to zinc amalgams, and they reduced uranyl salts in

either hydrochloric or sulfuric acid.^{280,288} Little if any trivalent uranium was formed.

(9) Reduction with Mercury. In solutions containing hydrochloric acid in sufficiently high concentration, uranyl ion is almost quantitatively reduced to uranium(IV) ion in a mercury reductor.²⁸⁹

(10) Reduction with Copper. It has been stated²⁹⁰ that, when uranyl sulfate is boiled in 3N to 4N sulfuric acid with a copper spiral in an apparatus from which air has been excluded, complete reduction to the quadrivalent state takes place in 20 to 45 min.

(11) Reduction with Aluminum and Magnesium. When a uranyl sulfate or chloride solution that is slightly acid is boiled with either magnesium or aluminum metal, reduction to uranium(IV) and uranium(III) occurs.²⁹² Air must be excluded after all the reducing metal is dissolved to prevent oxidation of the warm solution during cooling. Aluminum in the form of a spiral is convenient,^{291,292} or the aluminum can be suspended in a glass basket in a flask closed with a rubber stopper holding a bunsen valve.²⁹³ The method has been used chiefly for qualitative analysis of uranium.

(12) Reduction with Sodium Hyposulfite. It was found²⁹⁴ that sodium hyposulfite would reduce uranyl sulfate in mildly acid solution to uranium(IV) sulfate, which could be isolated by addition of alcohol. Other uranium(IV) salts (oxalate, arsenate, and phosphate) were prepared similarly. Sodium hyposulfite is a convenient agent for reducing uranium(VI) to uranium(IV) for chemical separations such as with cupferron, but it has little application in volumetric analysis. The reduction is best carried out in 4 to 8 per cent sulfuric acid,¹¹⁶ the solid $\text{Na}_2\text{S}_2\text{O}_4$ being stirred into the liquid. For the first 100 mg of uranium, 2.5 g of the reducing agent is required, but for each additional 100 mg of uranium, 0.6 g will suffice. The reaction is complicated, and some hydrogen sulfide is formed, as well as sulfur and sulfur dioxide.

(13) Reduction with Stannous Chloride. Stannous chloride similarly reduces uranyl salts, but the excess reducing agent is difficult to remove and makes the reaction useless for volumetric analysis.²⁹² Reduction with stannous chloride may be used, however, in chemical separations such as the precipitation of uranium tetrafluoride. Addition of stannous chloride to uranium(IV) solutions prevents air oxidation of the latter; this is a useful chemical in the precipitation of uranium(IV) oxalate.

(14) Reduction with Titanous Chloride or Sulfate. Titanous salts reduce uranium(VI) to uranium(IV) readily.²⁹⁵ This reaction has been used in the reductimetric titration of uranium as described below.

When used to reduce uranyl salts for oxidimetric titration the excess titanous compound may be removed by bismuth trioxide, Bi_2O_3 , which is reduced to the metal.²⁹⁶ The bismuth metal and excess oxide are filtered off, and the filtrate is titrated in the ordinary manner. The uranyl-tartaric acid complex is reduced by titanium trichloride to the uranium(IV)-tartaric acid complex.^{295,297}

(c) Oxidation to Uranium(IV). (1) Aeration. By aeration, trivalent uranium is rapidly oxidized to quadrivalent uranium, which is quite air-stable in cool acid solutions. Quadrivalent uranium in 5 per cent sulfuric acid has been exposed to air with occasional stirring for as long as 4 hr at 20 to 25°C with no apparent oxidation.⁷⁵ A precision and accuracy of ± 0.02 per cent have been obtained in the assay of the standard black oxide, MS-ST (see Sec. 3.3a), even though the time of aeration varied from 15 min for 0.64 g of uranium to 25 min for 0.85 to 1.7 g of uranium; a constant rate of aeration, approximately 130 ml of air per minute, was used, and all the solutions turned to the characteristic green color of uranium(IV) in less than 15 min.²⁴⁹ Results of investigations²⁹⁸⁻³⁰⁰ on the effect of varying acidity on the air oxidation of pure quadrivalent uranium solutions at room temperature are inconclusive; the previously reported relation²⁹⁸ was based on experimental results that do not agree with those given above for pure uranous solutions. The rate of aeration is not critical, but oxidation is slow if the solution is not agitated either by a rapid stream of bubbles or by stirring. Hot (60 to 80°C) uranous solutions are air-oxidized at an appreciable rate.^{75,301} Molybdenum seriously interferes with aeration. In solutions containing 0.4 g of uranium and 0.25 to 90 mg of molybdenum per 100 ml, molybdenum acts as a catalyst and causes the oxidation of uranium to go beyond the quadrivalent state during aeration; but if the molybdenum concentration is over 90 mg per 100 ml, complete oxidation of the molybdenum from the trivalent to the quadrivalent state by aeration is difficult and high results may be obtained for uranium (see reference 302). Nichols^{299,300} reported that the autooxidation of uranium(IV) chloride is markedly accelerated by traces of cupric ion. Ferric chloride has a very slight accelerating effect, but chlorides such as chromic, uranyl, or cobaltous have either negligible or no effect. Neither illumination of the solution nor increasing the glass surface in contact with the sample by addition of powdered glass has any effect. Heaney³⁰³ has shown that copper seriously interferes in the air oxidation of uranium(III) to uranium(IV). Although copper is precipitated in the Jones reductor it does not all stay in the amalgam; some is washed through with the reduced solution. It rapidly redissolves and causes the air oxidation of uranium to go beyond the quadrivalent state.

Kolthoff and Lingane³⁰⁴ reported that very dilute solutions of quadrivalent uranium (0.001N) in 5 per cent sulfuric acid appeared to be air-stable for at least 30 min. After air had been passed through this solution for 1 hr, 1 per cent of the uranium was oxidized to the hexavalent state. Pepkowitz²³⁶ reported that on a micro scale the reduced state was very susceptible to air oxidation. When air was blown through the solutions containing 1 mg of uranium and the potential of the system was followed electrometrically, there was a continuous rise in potential until the uranium(VI) state was reached, and at no time did the oxidation stop at the uranium(IV) state. However, micro quantities of uranium have been determined by titration in air after the solutions were passed through a micro Jones reductor and aerated briefly. Errors were less than ± 0.6 per cent for 0.5 mg (see reference 237) and ± 2 per cent for 0.1 mg of uranium (see reference 234). The addition to uranium of 10 per cent of its weight of nickel, cobalt, manganese, aluminum, zinc, or magnesium, 1 per cent calcium, or 20 per cent sodium does not interfere with its aeration.²⁰⁴

Procedure. The reduced uranium solution, which contains at least 4 per cent by volume of sulfuric acid and is free of molybdenum, copper, or other interfering substances, is aerated at 20 to 25°C with a rapid stream of fine bubbles of washed air for 15 min or until 5 min after the characteristic green color of quadrivalent uranium appears.

(2) Potentiometric Titration. (See Chap. 25 on "Electrometric Methods.") Several procedures call for potentiometric determination of the uranium (III)/(IV) end point. The oxidation to quadrivalent uranium may be accomplished by aeration in a cold solution^{200,274} or by titration with an oxidizing agent in a hot solution in a carbon dioxide atmosphere.^{2,301}

In titrations the precise end point of the uranium (III)/(IV) change is difficult to determine. It can be found if a 0.1N oxidizing reagent is used, but if the titrating increments are decreased by using a more dilute reagent, the drifts in potential become more and more dominant until they completely obscure the end point.²⁶¹ In titrations at approximately 80°C the interval between the two potential breaks corresponds stoichiometrically to the quantity of uranium present, but at room temperature the interval is somewhat too short. The first potential break probably corresponds not to the disappearance of trivalent uranium but to the disappearance of the adsorbed hydrogen layer on the platinum electrode. These correspond at high temperatures, 80°C, when hydrogen is rapidly oxidized by the titrant, but at low temperatures oxidation is slower, and there is a time interval before the electrode responds to the disappearance of trivalent uranium.²⁰⁰ In one modification²⁵⁷ trivalent uranium is oxidized to quadrivalent ura-

nium by the addition of chromic sulfate, and the chromium (II)/(III) break is used in place of the uranium (III)/(IV) break.

(3) Oxidation with Hydroxylamine. Trivalent uranium is oxidized to the quadrivalent state by hydroxylamine, and this method of oxidation has been used in some titrations employing ferric ion. However, more than a small excess of hydroxylamine in the presence of appreciable amounts of iron causes low results for uranium, owing to the oxidation of some iron(II) to iron(III) by hydroxylamine.^{237, 305, 306}

(d) Titration of Uranium(IV). (1) Titration with Ceric Sulfate. According to G. F. Smith³⁰⁷ cerium exists in solution as a "cerate anion" and when present in sulfuric acid should be called "sulfato-ceric acid." Direct titration of quadrivalent uranium in dilute sulfuric acid at room temperature with ceric sulfate gives a sluggish end point, and in semimicro titrations under these conditions the results are 1.0 to 2.6 per cent low.³⁰⁸ Sharp and satisfactory end points are obtained by titrating after the addition of excess ferric alum^{260, 308, 309} or ferric chloride³⁰⁴ or by heating at 50°C just before the end point is reached.^{310, 311} The solution must be protected from air if it is heated earlier than just before the end point is reached.³¹⁰ Titration with excess ceric sulfate followed by back-titration with ferrous sulfate is also very satisfactory (see references 235, 261, 308, and 312). The results obtained for 10-mg samples³⁰⁸ were within ± 0.1 per cent of the theoretical value when excess ceric sulfate followed by back-titration with ferrous sulfate was used and were 0.01 to 0.07 per cent high when ferric alum was added to the quadrivalent uranium solution before titration. The most satisfactory indicator is ferrous 1,10-phenanthroline sulfate (ferroin).³¹³ Birnbaum and Edmonds reported that the indicator dissociates rapidly at 50°C in 4N hydrochloric acid, and as a result the pink color fades before the end point is reached. Thus more indicator must be added.²⁵⁹ They recommended the addition of phosphoric acid to speed the uranium reaction and stated that the rate was too slow in the absence of this acid. Subsequently, phosphoric acid was also added in procedures using 4N sulfuric acid solutions.^{256, 314} Recently, Warf³¹¹ has reported that the oxidation of uranium(IV) perchlorate in dilute perchloric or sulfuric acid solutions is not catalyzed by small amounts of phosphoric acid, osmium tetroxide, or iodine chloride. However, the phosphoric acid concentration used by Warf was apparently not over one-tenth of that used by Birnbaum and Edmonds. Small amounts of nitric acid (about 1 to 5 per cent) do not interfere in ceric titrations.^{310, 315} Up to 100 mg of trivalent arsenic gives no interference in the direct titration at room temperature of a 300-ml solution containing 5 ml of phosphoric acid and 25 ml of sulfuric acid.³¹⁵

(2) Titration with Potassium Permanganate. Potassium permanganate is the classical reagent employed for the titration of uranium(IV) solutions and may be used either without an indicator or with one such as ferroin,^{71, 318, 317} or the end point may be determined by potentiometric methods.²⁵⁷ Uranium (50 to 500 mg) may be determined with an accuracy of 0.1 per cent.^{2, 75, 257}

Potentiometric titrations from uranium(III) to uranium(IV) and uranium(IV) to uranium(VI) must be carried out in a carbon dioxide atmosphere, and the temperature must be at least 80°C, at which temperature end points are sharp and equilibrium is reached rapidly. At 70°C equilibrium is poor in the vicinity of the end point. The presence of a large amount of iron causes decreased sharpness of the uranium (IV)/(VI) end point and increasing negative errors. In the titration of 0.36 g of uranium the error increased from 0.05 per cent with no iron to -0.35 and -2.0 per cent with 0.01 and 2.0 g of iron, respectively. Rapid titration in the presence of 2 g of iron gave no end point for uranium (IV)/(VI); several milliliters of saturated ammonium thiocyanate was added to serve as the end-point indicator, but the ferric thiocyanate color formed too slowly to be of use.²³⁹

(3) Titration with Potassium Dichromate. In order to obtain a good end point in this titration the quadrivalent uranium is usually oxidized with a ferric salt before titration.^{304, 308} Phosphoric acid is then added to complex ferric ion, and the acidity is adjusted with either phosphoric or sulfuric acid. Diphenylamine sulfonic acid gives more soluble oxidation products and a more pronounced color change than diphenylamine.³¹⁸ The titration is very sensitive to nitrate ions; no end point is detected when more than a few tenths of a gram of nitric acid is present.³¹⁹

Under carefully duplicated conditions an experienced analyst can obtain an accuracy of 0.1 to 0.2 per cent with the visual method.^{257, 320} A precision of 1 part in 3,000 may be obtained by either of two potentiometric-titration procedures that have been developed for high-precision work.^{249, 278} In one procedure a slight excess of solid dichromate, weighed to 0.03 mg, is added to the quadrivalent uranium solution, and after it has stood at least 15 min the excess is back-titrated with 0.01N ferrous sulfate. In the other procedure 0.1N potassium dichromate is added from a special jacketed 35-ml chamber buret, which can be read to 0.005 ml. After about five-sixths of the quadrivalent uranium has been oxidized, the remainder is oxidized by the addition of a slight excess of ferric alum, and then dichromate is added again until the ferrous ion is oxidized.^{274, 278}

Procedure (Visual).³²¹ About 300 ml of a solution containing 300 mg or less of quadrivalent uranium and at least 10 ml of sulfuric acid is

mixed with 20 ml of 4 per cent $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Then 15 ml of a 2 to 1 mixture of phosphoric and sulfuric acids is added. Eight drops of 0.01M sodium diphenylamine sulfonate³²² is added, and the solution is titrated slowly with 0.027N potassium dichromate, with constant stirring, until the pure green color changes toward a gray-green. Then the dichromate is added very slowly, 1 drop at a time, until the first permanent tinge of purple or violet-blue appears. The indicator consumes a little dichromate for its own oxidation,³²³ but no correction is necessary if the dichromate is standardized in the same manner against a solution of known uranium content.

Procedure (National Bureau of Standards Potentiometric).²⁴⁹ Solid potassium dichromate, National Bureau of Standards sample No. 136, weighed to 0.03 mg is added to the solution containing 0.65 to 1.7 g of quadrivalent uranium and 5 per cent sulfuric acid by volume. The amount of dichromate added is approximately 3 mg more than that calculated to be required to oxidize all the uranium. After standing at least 15 min the excess dichromate is titrated potentiometrically with approximately 0.01N ferrous sulfate solution [containing 3.92 g of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 1,000 ml of cool H_2SO_4 (1 to 19)], which is added from a 10-ml buret graduated to 0.05 ml. The end point is determined by means of a platinum-saturated calomel electrode system in connection with a vacuum-tube voltmeter.³²⁴ The ferrous sulfate solution is standardized each day against a weighed amount of dichromate. Vacuo corrections are made on the sample and dichromate weights.

Procedure (Purdue Potentiometric).²⁷⁴ The sample solution should contain 300 to 420 mg of reduced uranium in 1N sulfuric acid and no organic matter, nitrate, or iron. [Moderate amounts (100 mg) of chromic, cupric, nickelous, and chloride ions do not interfere.] A platinum electrode and a 0.5M potassium sulfate-mercurous sulfate half cell are placed in the solution and connected to a potentiometer. The solution is stirred and slowly aerated until the uranium (III)/(IV) break is detected, at which time the air is replaced immediately with pure nitrogen. Approximately 25 ml of standard 0.1N potassium dichromate (in 1N sulfuric acid) is added from a water-jacketed calibrated 35-ml chamber buret. Five milliliters of approximately 0.1N ferric alum [prepared by dissolving 48.5 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and diluting to 1 liter with 1N H_2SO_4] and 2 drops of 0.2 per cent barium diphenylamine sulfonate indicator are added, the solution is stirred 3 min, and the temperature of the buret is noted. The titration is continued cautiously until the indicator warns of the approaching end point and then is finished potentiometrically. The volume of dichromate is calculated to the nearest 0.005 ml by means of the second

differential of voltage to volume. The uranium content is calculated after subtracting a reagent blank and making the proper buret calibration and temperature corrections to 20°C.

(4) Titration with Ferric Solution. Ferric titrations of uranium(IV) solutions usually are carried out at elevated temperatures in order to speed the reaction. For the most accurate results air must be completely excluded. However, in some routine procedures, rapid titration is the only protection used against air oxidation.^{325, 326} End points are determined either visually in the presence of thiocyanate, potentiometrically, or amperometrically. If thiocyanate is used as an internal indicator, titration with ferric chloride must be carried out below 90°C to avoid decomposition of the red ferric thiocyanate.³⁰¹

The most accurate and precise ferric procedure is the ferric sulfate potentiometric titration in 4 to 6 per cent by volume sulfuric acid at 90 to 95°C under an atmosphere of carbon dioxide.^{327, 328} The accuracy and precision are ± 0.1 per cent or better²⁷⁸ in development and research work and ± 0.3 per cent in routine analysis.³²⁷ The accuracy is similar in 3 to 10 per cent by volume perchloric acid (70 per cent)³⁰⁶ but a little lower with 0.1N ferric chloride in hydrochloric acid solutions;^{237, 258} the optimum hydrochloric acid concentration is 15 to 30 per cent, by volume. Chlorides appear to interfere with the ready establishment of an equilibrium electrode potential.²⁵⁷ Nitrates and fluorides should be absent.³⁰⁶ Copper,²⁷⁷ tungsten, molybdenum, and vanadium²³⁷ interfere seriously. Small amounts of tin produce a slight positive error.²⁷⁷ Very large amounts of zinc or chromium tend to reduce the sensitivity of the indicator platinum electrode during titration.²⁷⁶ Large amounts of iron or cadmium²⁷⁶ and moderate amounts of chromium, manganese, nickel, aluminum, or lead do not interfere, although large amounts of iron do have a depressing effect on the size of the uranium (IV)/(VI) break.²⁵⁷ The uranium (III)/(IV) system frequently yields an unsatisfactory end point. More consistent end points are obtained by replacing the uranium (III)/(IV) system with the chromium (II)/(III) or the titanium (III)/(IV) system.²⁵⁷ The uranium (III)/(IV) system yields an end point at 0.5 volt. The addition of titanium(IV) replaces the uranium (III)/(IV) system by titanium (III)/(IV), which yields a very satisfactory and reproducible end point at 0.1 volt. The amount of titrant consumed between the titanium (III)/(IV) and the uranium (IV)/(VI) end points corresponds to the uranium (IV)/(VI) titer. However, in the presence of titanium the uranium (IV)/(VI) end point is more difficult to observe because the potentials appear to be very slowly established. The addition of chromium(III) and the resulting substitution of the chromium (II)/(III) system, which give an end point at 0.4 volt, yield sharp end points and

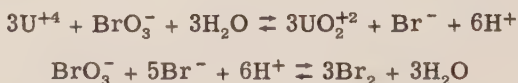
readily established potentials throughout the titration. A potentiometer must be used for determining the end points.^{301, 328} The rate of oxidation of uranium(IV) by iron(III) in 5 per cent sulfuric acid has been studied by means of the absorption maximum of uranium(IV) at 650 m μ . Since it was found that the rate of oxidation is faster than the time of addition and absorption measurements (approximately 1 min), it appears that titrations at room temperature would be feasible if some way could be found to speed the rate of establishment of potential equilibrium at the electrode.³⁰⁶

Procedure (Potentiometric).^{327, 332} The solution containing 300 to 500 mg of trivalent and quadrivalent uranium, and no nitrate or its reduction products—chloride, copper, tungsten, molybdenum, or vanadium—in approximately 225 ml of 5 per cent by volume sulfuric acid is collected in a covered lipless beaker. The covered beaker is affixed immediately to the potentiometric titration apparatus, and a current of carbon dioxide is passed over the surface of the solution at an approximate rate of 500 ml per minute. Ten milliliters of a chromic sulfate solution containing 0.1 g of chromium is added, and the sample is stirred and heated to 90 to 95°C. Then the solution is titrated potentiometrically with 0.1N ferric sulfate, in 5 per cent sulfuric acid. The titrant consumed between the chromium (II)/(III) and the uranium (IV)/(VI) potential breaks is the uranium (IV)/(VI) titer. A Leeds & Northrup potentiometer with a high-temperature calomel electrode and a 20- to 25-gauge³⁰⁶ smooth platinum-wire electrode were used. The platinum electrode should be cleaned with hot chromic acid solution after each titration to assure most satisfactory operation.²⁵⁷

Amperometric titrations of uranium(IV) with iron(III) may be made at room temperature under an atmosphere of nitrogen (see references 241 and 329-331). In the procedure used by Kwiatkowski et al.³³¹ the uranium is reduced with a chromous solution and titrated in a 5 per cent sulfuric acid medium by using a large high-temperature saturated-calomel-dropping-mercury-electrode system in conjunction with a shunted galvanometer.^{241, 330} Titrations are carried out at room temperature under an atmosphere of nitrogen, and the sample is stirred after each addition of iron(III). The use of a mercury pool as anode is not practicable because mercury slowly reduces iron(III) and the pool would have to be protected, for example, by means of a layer of redistilled chloroform. Nitrate,³³¹ copper, and vanadium interfere with the titration. However, molybdenum and titanium apparently do not interfere. Results obtained in macro titrations (200 to 500 mg of uranium) were consistently high—about 0.3 to 0.8 per cent; these high results may have been due to incomplete attainment of

chemical equilibrium. Errors of -1.8 to 2.8 per cent were obtained for 5- to 50-mg quantities of uranium. With 0.5- to 4-mg quantities of uranium, errors increased to as much as 16 per cent; they were increased even further by the use of a 0.01N ferric sulfate solution, owing to increased uncertainty of the end point.²⁴²

(5) Titration with Potassium Bromate.³³³ The direct titration of quadrivalent uranium in hydrochloric acid with potassium bromate, using the bleaching of methyl orange as an indicator, involves the following reactions:



Because the first reaction proceeds very slowly and also because the rates of the reactions are not greatly different, a premature end point is obtained. The first reaction is not catalyzed by the individual addition of cupric chloride, ammonium molybdate, iodine monochloride, or various concentrations of hydrochloric or sulfuric acid. The addition of excess bromate and, after standing, the addition of excess potassium iodide and titration of the liberated iodine are also unsatisfactory.²³⁹ However, if a ferric solution is added to the uranium(IV) solution, which has been adjusted to contain 20 per cent hydrochloric acid and which contains cupric chloride as a catalyst, the reduced iron can be titrated with potassium bromate. Nickel, large amounts of copper, and reduced substances such as iron, vanadium, or molybdenum which might be titrated should be absent. Results tend to be high, probably owing to the loss of bromine. Errors up to 0.4 per cent are obtained but may be minimized by frequent shaking.

Procedure.³³³ The solution containing 90 to 450 mg of quadrivalent uranium in about 200 ml of 2 per cent sulfuric acid is placed in a 500-ml glass-stoppered Erlenmeyer or iodine flask and cooled to 10°C. After addition of 10 ml of 0.5M $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 75 ml of cold hydrochloric acid, 2 ml of 10 per cent $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 2 drops of 0.1 per cent methyl orange, the solution is titrated with 0.1N potassium bromate until the red color changes suddenly to yellow or yellow-orange. If the odor of bromine is noticed during the titration, the flask should be stoppered and shaken well to cause the bromine to dissolve and react. Usually the red color fades more or less during the titration. When this occurs additional indicator is added, 2 drops at a time, and the titration is continued to a sharp color change. At the true end point the addition of 1 drop of methyl orange is followed by a rapid fading of the red color.

(e) Titration of Uranyl Solutions. (1) Titration with Chromous Solution. Lafferty and Winget²³³ recommend the use of the chromous titration of Flatt and Sommers²⁰⁵ in order to eliminate the pretitration reduction of uranyl solutions and to avoid the interference of fluoride ion. Errors obtained in 28 determinations of 100 to 500 mg of uranium by the following procedure ranged from -0.8 to $+1.2$ per cent with an average of ± 0.3 per cent.

Procedure.²³³ A 0.1N chromous sulfate solution is prepared and stored under carbon dioxide as described by Stone and Beeson.³³⁴ A sample containing 100 to 500 mg of uranium and no ferric, cupric, mercuric, nitrate, or other ions that oxidize chromous sulfate, is dissolved in 100 ml of distilled water and 10 ml of sulfuric acid. If there is any doubt as to the valence state of the uranium present, bromine water is added and the solution is boiled until all the bromine is expelled. A stirrer and the electrodes of a Serfass titrimeter³³⁵ are immersed in the solution, the latter is heated to about 70°C , and a slow current of carbon dioxide is passed over the beaker. The sensitivity control on the titrimeter is set at 3 and the eye is closed. Standard chromous sulfate is added slowly until 1 drop opens the eye completely. The chromous sulfate is standardized in triplicate and checked at least once a week by the following procedure: From 25 to 35 ml of 0.100N potassium dichromate is measured accurately from a buret into a 250-ml beaker and diluted to 100 ml with distilled water. Ten milliliters of sulfuric acid is added, the solution is boiled gently for 3 to 5 min, and the electrodes and stirrer are immersed in the solution. The sensitivity control on the titrimeter is set at 1 and the eye is closed. While a slow current of carbon dioxide is passed over the solution, the solution is titrated as above with the chromous sulfate.

(2) Titration with Phosphate. By reversing one of the classical volumetric methods of determining phosphates, uranium can be determined. Phosphates may be titrated with uranyl acetate or nitrate by using potassium ferrocyanide, sodium salicylate, or sodium 2-hydroxy-5-methylbenzoate (2,5-cresate)³³⁶ as outside indicator.^{337, 338} A uranyl phosphate of the type UO_2MPO_4 (M univalent cation) precipitates. The method is not characterized by great accuracy, but it is rapid and serves when rough results are satisfactory. In this titration it is important to standardize the phosphate solution under the same conditions under which the determination is carried out because various ions such as the alkalis, the alkaline earths, aluminum, acetate, and citrate modify the end point. Slightly acid acetate solutions are titrated at 80 to 90°C . The end point may also be determined electrometrically.³³⁹

Procedure.²⁰⁸ A solution of potassium dihydrogen phosphate, approximately 0.1M, is standardized against a standard uranyl nitrate solution under the same conditions as those under which the titration is performed. The uranyl solution to be titrated, which should contain 50 to 400 mg of uranium and no copper, is treated with dilute ammonium hydroxide until a permanent precipitate forms; then barely enough acetic acid is added to redissolve it. A large excess of acetic acid should be avoided. The solution is diluted to 50 to 200 ml, depending on the amount of uranium, heated to about 90°C, and cautiously titrated with the potassium dihydrogen phosphate solution with vigorous stirring. The titration is continued until a drop of the solution fails to give a positive test with a little powdered potassium ferrocyanide on a white spot plate. Several titrations should be run. Some practice is necessary for acceptable results.

(3) Titration with Sodium Hydroxide. By employing an empirical factor, uranium may be determined by potentiometric titration with sodium hydroxide.³⁴⁰ The uranium must be present in the hexavalent state, and any ions capable of forming insoluble precipitates with sodium hydroxide must be absent. The presence of acid does not interfere since two distinct points of inflection, one for the acid and one for the uranium, are obtained. In fact, the amount of acid present may also be determined from the same titration. The method is very useful for the routine analysis of such solutions as uranium hexafluoride in water, uranyl nitrate in nitric acid, and uranyl sulfate in sulfuric acid. Powell and Newton³⁴¹ reported that uranium tetrabromide solutions may also be titrated with sodium hydroxide. Harris¹⁰¹ reported that electrometric titrations of uranyl chloride with sodium hydroxide do not give smooth curves and are greatly influenced by the uranium concentration and by the time the solution is permitted to stand. He states that basic salts such as $\text{UO}_2(\text{OH})_{1.1}\text{Cl}_{0.9}$ precipitate.

Procedure.³⁴² A sample containing 30 to 500 mg of uranium is dissolved in 100 ml of water and transferred to a titration flask equipped with a stirrer, calomel electrode, and glass electrode. The titration is made with standard 0.1N sodium hydroxide, and the pH readings are noted as soon as possible after each addition. The point of inflection in the titration curve corresponding to the neutralization of the acid occurs between pH 4.5 and 7, depending on the $\text{UO}_2^{++}/\text{acid}$ ratio. However, the point of inflection corresponding to the reaction between UO_2^{++} and sodium hydroxide occurs at pH 9.0 to 9.1. The amount of uranium present is calculated from the amount of sodium hydroxide that is used between the two points of inflection by assuming that 2.22 moles of sodium hydroxide is required for 1 mole of uranium. This factor has been found to be constant over a large range of uranium and acid concentrations.

(4) Titration of the Quinolate with Bromate-Bromide Solution. Uranium may be determined by titrating the 8-hydroxyquinoline (oxine) in the precipitate that is formed when uranium is separated with this reagent.¹²⁰ When the compound $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$ is dissolved and the oxine is titrated by the bromate-bromide method, errors of about 1 per cent are obtained on a 5-mg sample of uranium (see reference 343). Results obtained for 25 to 100 γ of uranium by cerate oxidation of uranyl quinolate were unsatisfactory.³⁴³

Procedure. The $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$, when precipitated, filtered, and washed as described in Sec. 2.2 of this chapter, is dissolved in approximately 2N HCl. The filter is washed, and the solution plus washings is transferred to an iodine flask. The solution is diluted to 50 to 75 ml with 2N HCl, and 1 g of KBr and 2 to 4 drops of 0.1 per cent solution of methyl red (sodium salt) are added. The solution is slowly titrated with standard KBrO_3 (0.1N) until the color changes from orange to yellow. Two or three milliliters more of the KBrO_3 is added, and the mixture is allowed to stand a few minutes in the stoppered flask. A gram of KI is added, and the iodine is titrated with $\text{Na}_2\text{S}_2\text{O}_3$ (0.1N). Instead of titrating with KBrO_3 , an amount that is known to be an excess may be pipetted in, and the excess back-titrated as usual.

(f) Micro Methods. Milligram quantities of uranium have been determined by micro titrations with potassium permanganate,³¹⁶ ceric sulfate (see references 234-236, 238, and 250), or potassium dichromate.²³⁷ Errors of only ± 0.6 per cent for 0.5 mg²³⁷ or ± 2 per cent for 0.1 mg^{234, 235} of uranium have been obtained by using micro modifications of standard macro procedures. On the other hand, Pepkowitz²³⁶ reported that micro titrations should be made in an inert atmosphere in order to avoid air oxidation of quadrivalent uranium; for convenience and also to eliminate the possibility of air oxidation during transfers the complete determination was done in a special titration cup. An average recovery of 99.9 per cent was obtained on samples ranging from 0.1 to 2.5 mg; errors were as great as ± 0.5 per cent for 1 mg and -1.8 per cent for 0.1 mg of uranium.

Procedure (Without Carbon Dioxide Atmosphere).²³⁷ The sample of about 5 ml, which is 5 per cent in H_2SO_4 , is passed through a small Jones reductor. It is washed through the reductor with 5 ml of 5 per cent H_2SO_4 and 2 ml of H_2O . After the reduction the solution is aerated by swirling for a short time. Sufficient H_2SO_4 is added to make the solution 10 per cent in H_2SO_4 (by volume). The solution of about 10 to 15 ml is titrated with 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$, delivered from a Kirk micro-buret by using 0.1 ml of 0.2 per cent diphenylamine sulfate as the indicator.

Procedure (With Carbon Dioxide Atmosphere).²³⁶ The sample is dissolved in nitric acid, and the solution is transferred to a 10-ml platinum crucible. Two drops of sulfuric acid is carefully added down the side of the crucible. The solution is heated under an infrared lamp until the fumes of sulfuric acid are evident. The crucible is

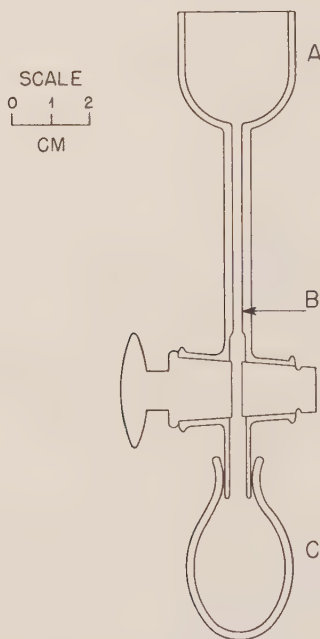


Fig. 1.7—Titration assembly. A, titration cup; B, capillary tube; C, rubber bulb.

transferred to a small hot plate and heated until all the acid has been fumed off. Care must be taken to avoid spattering, and the residue must not be ignited. The uranyl sulfate is taken up in 1 to 2 ml of water and transferred quantitatively to the titration cup (cf. Fig. 1.7). The titration cup is placed on a stand and a stream of carbon dioxide is adjusted so that it will impinge on the surface of the solution to be placed in the cup.

The rubber bulb is filled completely with deaerated water and is attached to the cup with the stopcock open. The bulb is carefully compressed so that the water is forced into the stem of the cup, displacing all the air in the stem.

One to two milliliters of zinc amalgam is run into the cup, and then the uranyl sulfate solution, taken up in 1 to 2 ml of water, is

transferred into the cup. No more than 3 to 4 ml of water should be used for the transfer. This is necessary because the final volume should not be over 5 to 6 ml. The stirrer, a flattened glass rod, is adjusted so that both the amalgam and the solution are agitated. The carbon dioxide stream is kept running at all times during the determination. The solution should be approximately 0.05N in H_2SO_4 , and 2N H_2SO_4 is added if necessary. The solution is reduced for 5 min. After reduction, sufficient 0.1N potassium permanganate (usually 1 drop) is added to make the solution pink, and it is reduced again for 10 min after the disappearance of the pink color. If during this second reduction the solution becomes turbid owing to the formation of manganese dioxide, a drop of 2N sulfuric acid is added, and sufficient time is allowed for reduction of the manganese dioxide. If the turbidity does not disappear another drop of acid is added. Following the 10-min reduction period the stirrer is stopped, and 2 to 3 ml of carbon tetrachloride is added. The stopcock is carefully opened, and the bulb is gently squeezed to force water around the amalgam. The pressure on the bulb is released, and the amalgam is allowed to run down into the bulb. This operation is repeated until all the amalgam is in the bulb and the carbon tetrachloride is drawn into the capillary. At this point there should be a layer of carbon tetrachloride in the bottom of the cup and the reduced solution above. The stirrer is raised, carefully so as not to agitate the carbon tetrachloride layer too violently, and is washed with 1 ml of deaerated water. Exactly 20 microliters of orthophenanthroline ferrous complex indicator (0.01M) is added, and the microliter pipet is washed out because these pipets are usually calibrated "to contain." During the second reduction period a micro weight buret is filled with standard ceric sulfate and weighed. After the indicator is added, the stirrer is started and the solution is titrated to a sharp change from red to colorless (or a very light blue). The ceric solution is added slowly near the end point, very small increments being used. The end point under proper conditions of acidity is a sharp color change, which is stable for 5 min. The buret is then reweighed, and the difference is the weight of ceric sulfate solution used in the titration.

3.4 Spectrophotometric and Colorimetric Methods. The determination of uranium by colorimetric and spectrophotometric methods has been used extensively. These methods are based on the light absorption of (1) uranous, or uranyl ions in aqueous or nonaqueous solvents, or as a gas in the gaseous phase; (2) inorganic compounds or complexes of uranium in aqueous solution; (3) organic compounds or complexes of uranium in aqueous or nonaqueous solutions.

(a) Uranium Ion in Aqueous or Nonaqueous Solvents. In many of the various phases of the work in which uranium was utilized, it was

essential to know the state of oxidation of the element. It was in connection with these uses that the greatest application was made of the light absorption of the uranium(IV) and uranyl compounds in inorganic and organic solvents.

Absorption spectra of uranium(III), uranium(IV), and uranium(VI) compounds have been obtained³⁴⁴⁻³⁴⁸ with various anions. Scott and Dixon³⁴⁴ have determined uranium in leach liquor by measuring the absorption at 410 m μ in phosphoric acid solution. Allen³⁴⁸ has shown that the absorption of uranium(IV) solution is dependent on pH, anion concentration, and the nature of the anion. In order to avoid interference from various ions, a phosphoric acid solvent medium has been used.^{346,349} Figure 1.8³⁴⁶ shows the absorption of uranium(IV) and uranium(VI) in concentrated phosphoric acid. The variation in the absorption of uranium(IV) at 600 to 700 m μ , with acid concentration as shown in Figs. 1.8 and 1.9 is much greater in a hydrochloric acid medium than in a phosphoric acid medium; this is one of the reasons that phosphoric acid has been used as a solvent in analytical methods.³⁴⁹ Concentrated uranium nitrate solutions have been analyzed for their uranium content from transmittancy measurements at 410 m μ , which is the wavelength of maximum absorption.^{347,350} The uranium(VI) content of solutions has been determined by extracting the uranium with diethyl cellosolve.³⁵¹ Uranyl fluoride may be extracted with methyl alcohol from green salt, UF₄.³⁵² The uranium tetrachloride content of gases can be determined by measuring the absorbency of the gaseous mixture at about 310 m μ , using a mercury lamp with filter as a light source and a photomultiplier tube for intensity measurements.³⁵³

Most of the above methods were developed for a certain determination and are not intercomparable. The determination of uranium(VI) and uranium(IV) is more readily carried out in phosphoric acid as a medium.³⁴⁹

(1) Phosphoric Acid Solution Method.³⁴⁹ The problem of determining uranium(IV) and uranium(VI) in solutions of compounds such as commercial uranium oxide is complicated by the fact that uranium(IV) shows some absorption over the entire wavelength range at which uranium(VI) absorption may conveniently be measured. The uranium(VI) ion, however, shows no absorption at 630 m μ ; therefore uranium(IV) may be measured without interference in mixtures of the two ions. To obtain the uranium(VI) concentration the optical density of the solution of the two ions is measured at 410 m μ and corrected to eliminate the uranium(IV) contribution to the optical density by use of the expressions

$$D_{410} \text{ for U(VI)} = D_{410} \text{ (measured)} - D_{630} \times R$$

$$R = \frac{D_{410}}{D_{630}} \text{ for pure U(IV) solution}$$

where D_{410} is the optical density at 410 $m\mu$ and D_{630} is the optical density at 630 $m\mu$. The constant R should be independent of uranium(IV) concentration, because the uranium(IV) solution has been shown to obey Beer's law over the concentration range used. In actual practice, however, R appears to vary slightly with the particular type of compound being measured. Since it is rather difficult to prepare a uranium(IV) compound free from traces of uranium(VI), the value of R obtained for any particular uranium(IV) compound may be uncertain. In actual practice it would seem best to determine a value for R that would best fit the particular compounds. This may be done by analyzing the material for uranium(IV) by volumetric methods.

In general, the analysis for uranium(IV) in a mixture is accurate to within 1 per cent. The accuracy of the uranium(VI) analysis depends on the uranium(VI) content of the sample. Small errors in the correction factor R can produce large errors in the uranium(VI) value when the uranium(VI) content is low.

Procedure. A sample of the uranium compound weighing 0.5 to 1.0 g is dissolved by heating in a small amount of concentrated phosphoric acid, and after it is cooled the solution is diluted to 100 ml with phosphoric acid. The transmittancy of the solution is measured at 410 and 630 $m\mu$ with phosphoric acid in the comparison cell. The uranium(IV) and uranium(VI) contents are obtained from the above expressions.

(2) Nitrate in Aqueous Solution Method.³⁵⁰ It is possible to determine the amount of uranium in concentrated uranyl nitrate solutions to within 5 per cent by measurement of the transmittancy at a wavelength of 410 $m\mu$, which is the wavelength of maximum absorption in the visible range. Solutions of pure uranyl nitrate in water at concentrations of 0.005 and 0.030 g per milliliter give transmittancies of 72.8 and 16.4 per cent, respectively. These values lie on a straight line passing through 100 per cent at zero concentration; however, the slope is not sufficiently great to permit high accuracy.

(3) Diethyl Cellosolve Solution Method. A rapid method for the determination of uranium in a solution that contains many highly colored ions such as iron, copper, nickel, and chromium was developed using diethyl cellosolve to extract the uranium(VI) from a saturated ammonium nitrate solution. The optical density of the diethyl cellosolve solution was measured at 430 $m\mu$.³⁵¹ Chlorides

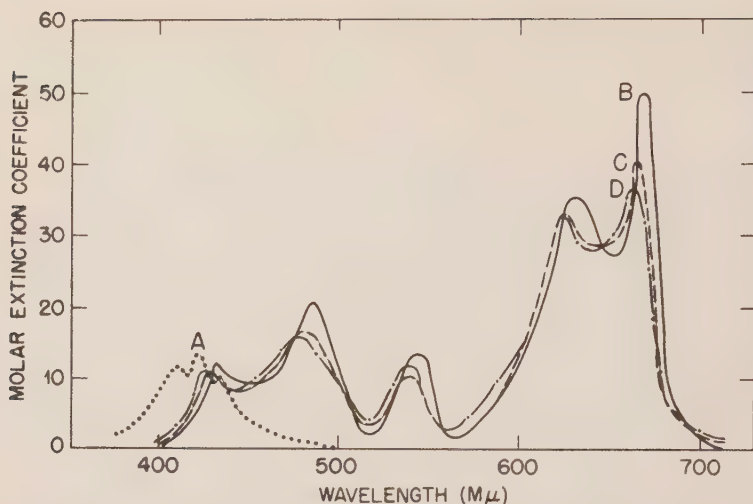


Fig. 1.8—Absorption spectra of uranium(IV) and uranium(VI) in phosphoric acid. Curve A shows uranium(VI) in H_3PO_4 (conc.); curve B shows uranium(IV) in H_3PO_4 (conc.); curve C shows uranium(IV) in H_3PO_4 (1 to 1); and curve D shows uranium(IV) in H_3PO_4 (1 to 5). All measurements were made with the Beckman spectrophotometer using 1-cm absorption cells.

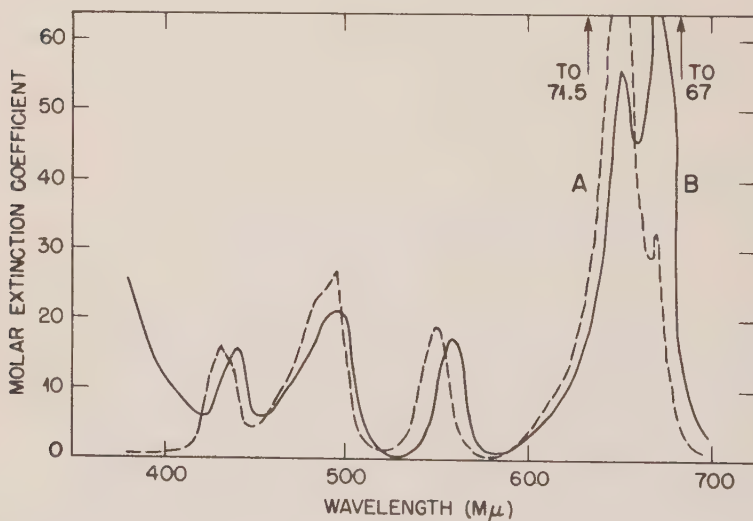


Fig. 1.9—Absorption spectra of uranium(IV) in hydrochloric acid solution. Curve A shows uranium(IV) in HCl (conc.), and curve B shows uranium(IV) in HCl (1 to 1). All measurements were made with the Beckman spectrophotometer using 1-cm absorption cells.

interfere because ferric chloride is extracted by the diethyl cellosolve. Sulfates, if present, will cause incomplete extraction.

The data suggest that for amounts of uranium greater than 100 mg per 10 ml of sample the method is capable of giving an accuracy of 5 per cent. A careful operator is required to obtain good results. The slope of the optical density-concentration curve is so low, 0.00034, that the method is only approximate.

Cellosolve Reagent. Six liters of redistilled commercial cellosolve is treated with a saturated ammonium nitrate solution (1 kg of salt plus 500 ml water). A little solid ammonium nitrate is added to maintain saturation. Twenty-five milliliters of nitric acid is added per liter of cellosolve, and the mixture is well stirred. The pH of the aqueous solution is determined, and nitric acid is added; the mixture is stirred after each addition until the pH of the aqueous solution becomes zero. The cellosolve is decanted, filtered, and stored.

Procedure.³⁵¹ A 10-ml sample is pipetted into a 150-ml beaker, and ammonia gas or ammonium hydroxide is added until the pH of the solution is 0. Solid silver nitrate is added in excess, the solution is filtered on a sintered-glass funnel, and the residue is washed with a small amount of nitric acid solution (pH 0). The final volume should be nearly 20 ml. The filtered solution is then saturated with ammonium nitrate by using 40 g of NH_4NO_3 per 20 ml of liquid. The solution is extracted in a separatory funnel with three 50-ml portions of cellosolve reagent. The mixture is shaken 3 min each time and allowed to stand 3 to 5 min before draining. The stopcock bore is left full of aqueous solution rather than cellosolve each time. The first two extracts are poured into a 100-ml volumetric flask, diluted to the mark with cellosolve reagent, and well mixed. The third extract is reserved in a stoppered 125-ml Erlenmeyer flask. The optical density of the first two extracts is measured at $430\text{ m}\mu$ after the cellosolve solution is filtered, discarding the first 10 ml that goes through the paper. Cellosolve reagent is used in the comparison cell. The optical density of the third extract is measured after it is filtered as above, and the value for the first two extracts is corrected accordingly. The weight of uranium in the sample is taken from a calibrated chart that has been obtained in the same manner.

(4) Oxyfluoride in Methyl Alcohol Method.³⁵² Uranium oxyfluoride is soluble in methyl alcohol, whereas uranium tetrafluoride is not. The alcohol solution has a maximum absorption at $420\text{ m}\mu$ and follows Beer's law. It is necessary to grind the commercial UF_4 in order to liberate all the uranium oxyfluoride that may be trapped in the grains. The method is capable of good precision with an accuracy of 1 to 2 per cent. The slope of the transmittancy-concentration curve is low

as in the diethyl cellosolve method. The range used was 10 to 130 mg of uranium oxyfluoride.

Procedure.³⁵² The sample of commercial UF_4 is ground for 60 min in a mechanical grinder. A 5-g sample is introduced into a 50-ml thick-walled Erlenmeyer flask, which is fitted with a ground-glass stopper, and 20 ml of absolute methyl alcohol is pipetted into the flask, which is then tightly stoppered. The flask is placed in a water bath maintained at 55°C for 1 hr and is shaken vigorously at intervals of 10 to 15 min. The solution is cooled, decanted into a centrifuge tube, and centrifuged for 10 min at 1,500 rpm. The transmittancy of the clear solution is measured at $420\text{ m}\mu$ with methyl alcohol in the comparison cell. (The transmittancy-concentration curve was made from uranium oxyfluoride, which was extracted as above from commercial UF_4 and analyzed by volumetric means, and also from uranium oxyfluoride made from uranium trioxide and hydrofluoric acid.)

(b) Inorganic Compounds or Complexes of Uranium. Of the various inorganic reagents used for the colorimetric determination of uranium the one used to the greatest extent has been alkaline peroxide.

(1) Determination by Means of Peroxide. The use of peroxide as a colorimetric reagent for uranium is well known. Although not the most sensitive, it has fewer interferences than other methods. Rosenheim and Daehr³⁵⁴ found that hydrogen peroxide, when added to a uranyl solution that had been made alkaline with sodium or ammonium carbonate, gave a yellow color that varied directly with the uranyl ion content. Hackl³⁵⁵ determined uranyl ion in sodium carbonate solution by using hydrogen peroxide. Cassidy³⁴⁷ investigated the photometric determination of uranium as the nitrate, as the carbonate complex, and as the carbonate complex with peroxide. The conclusion reached was that the carbonate complex with peroxide was much more sensitive than the other two methods, but that the intensity of color increased with increase in amount of alkali and simultaneously shifted the quality of color toward the red. Rodden and coworkers^{356, 357} advocated the use of sodium peroxide and sodium hydroxide as giving more reproducible conditions and eliminating the interference of vanadium. Sodium carbonate and hydrogen peroxide,³⁵⁷⁻³⁶¹ as well as sodium hydroxide and peroxide,^{357, 362-365} have been used to determine uranium. Solutions of uranium have been analyzed by adding sodium hydroxide and hydrogen peroxide to a sodium carbonate solution of the test material.^{173, 366, 367}

The use of ammonium hydroxide with peroxide has been advocated³⁶⁸ because the color intensity is higher in the presence of ammonium sulfate than when sodium hydroxide is employed. Ammonium carbonate has been used³⁶⁹ to obtain the desired alkalinity with the peroxide method in the presence of fluoride ions.

Peroxide in acid medium may be used^{173,370,371} for the determination of uranium. This method has the distinct advantage that chromium, which interferes seriously in the alkaline peroxide method, causes no trouble.

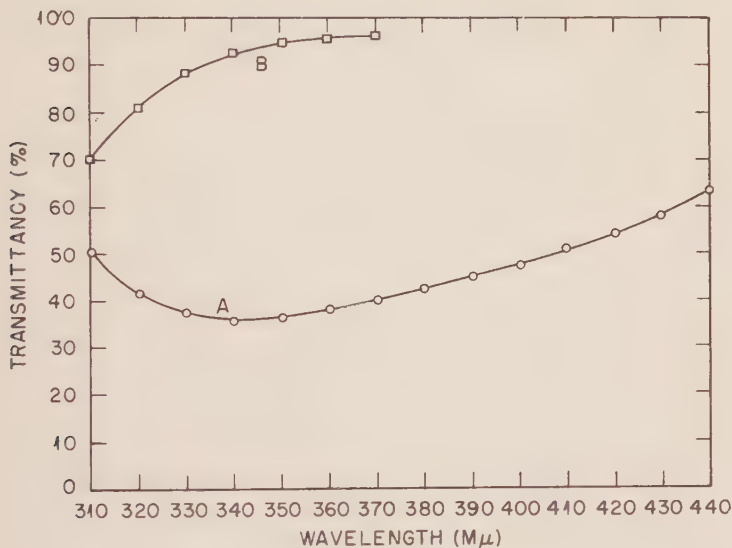


Fig. 1.10—Spectral transmittancy of uranium-peroxide-sodium carbonate solution. Curve A: A solution containing 5 mg of U_3O_8 , 5 ml of 20 per cent Na_2CO_3 , and 1 ml of 30 per cent H_2O_2 was prepared and diluted to 100 ml. The transmittancy was measured against a reagent blank. Curve B: The reagent blank was measured against distilled water. All measurements were made with a Beckman spectrophotometer using 2-cm cells.

(2) Basic Peroxide Method. The absorption of radiant energy by uranyl alkaline peroxide solutions has been investigated (see references 172, 173, 347, 357, 364, and 372). The spectral transmittancy¹⁷² as shown in Figs. 1.10 and 1.11 indicates that in both sodium carbonate and sodium hydroxide solutions there is a definite minimum at 340 mμ.

The maximum sensitivity for the determination of uranium is at 340 mμ, but certain factors affect measurements at this wavelength. The effect of peroxide on the absorption has been studied.^{173, 347, 366} Figure 1.12 shows the effect of varying amounts of peroxide on the transmittancy of an alkaline solution.¹⁷² It may be noted that hydrogen peroxide and sodium hydroxide solutions alone, in the concentrations used, have little absorption. When they are mixed the absorption increases considerably. The absorption of a sodium peroxide solution

is shown; this is similar to that of the hydrogen peroxide-sodium hydroxide mixture. Accurate measurements at $340\text{ m}\mu$ would, therefore, require close control of the peroxide concentration. In most work, measurements have been made in the region 400 to $440\text{ m}\mu$, in

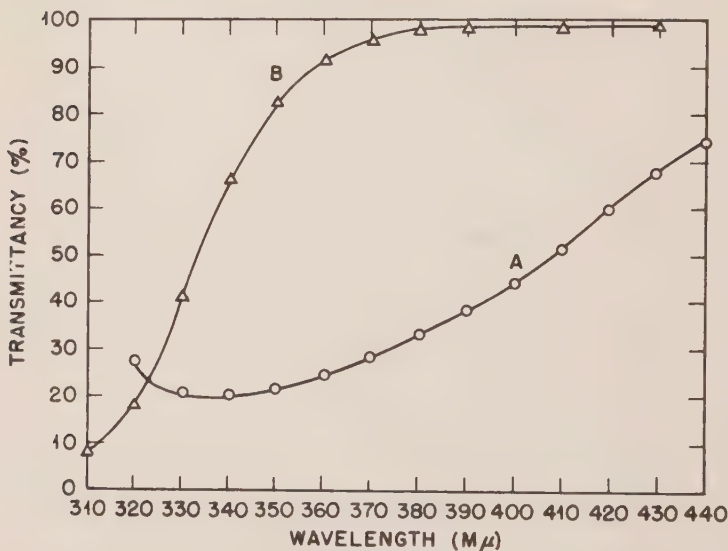


Fig. 1.11—Spectral transmittancy of uranium-peroxide-sodium hydroxide solution. Curve A: A solution containing 5 mg of U_3O_8 , 1 g of sodium hydroxide, and 1 ml of 30 per cent H_2O_2 was prepared and diluted to 100 ml, and the transmittancy was measured against a reagent blank that contained all the above except the U_3O_8 . Curve B: The above reagent blank was measured against distilled water. All measurements were made on a Beckman spectrophotometer using 2-cm cells.

which region the peroxide-concentration effect is eliminated (see references 173, 357, 364, and 366). This region is such that a filter photometer may be used.

The experiments of Cassidy³⁴⁷ showed that the sodium carbonate concentration affected the transmittancy of the complex. Further work¹⁷³ (as shown in Fig. 1.14) indicated that there was no increase in the transmittancy after the pH of the sodium carbonate solution was increased to 12 by the addition of sodium hydroxide. The optical density curve at pH 12 is shown in Fig. 1.15. The wavelength of maximum optical density is at $340\text{ m}\mu$, the same as found with sodium hydroxide alone. Arnold and Pray³⁷³ mentioned that a certain minimum quantity of ammonium carbonate and hydrogen peroxide is necessary for full development of color.

The stability of the complex is best shown by Table 1.3. Solutions containing varying amounts of uranium with 1 ml of 30 per cent hydrogen peroxide, 5 ml of 20 per cent sodium carbonate, and sufficient sodium hydroxide to establish a pH of 11 to 13 were diluted to 100 ml,

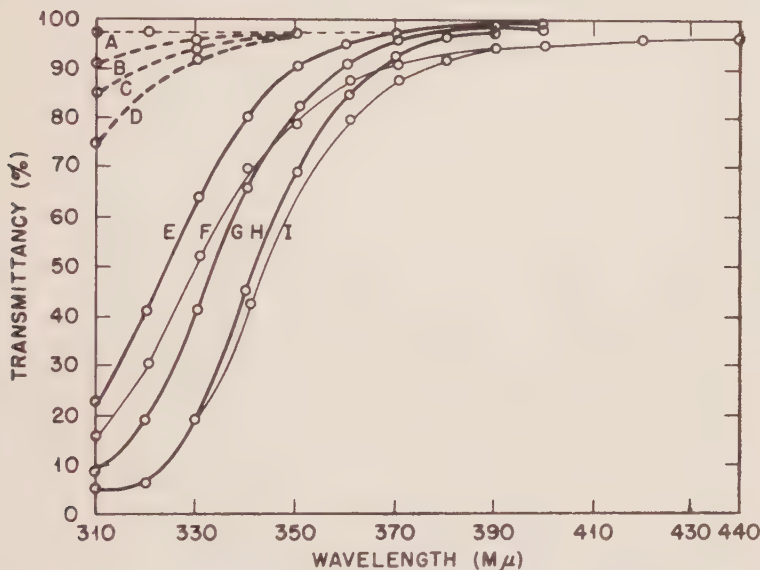


Fig. 1.12—Spectral transmittancies of hydrogen peroxide, sodium hydroxide, and sodium peroxide solutions. Curve A, 1.0 g of sodium hydroxide per 100 ml; curves B, C, and D, 0.5, 1.0, and 2.0 ml, respectively, of 30 per cent hydrogen peroxide per 100 ml of solution; curves E, G, and H, 1 g of sodium hydroxide plus 0.5, 1.0, and 2.0 ml, respectively, of 30 per cent hydrogen peroxide per 100 ml; curves F and I, 0.5 and 1.0 g, respectively, of sodium peroxide per 100 ml. All solutions were measured against water with a Beckman spectrophotometer using 2-cm cells.

and the optical density was measured at different time intervals.¹⁷³ The color of the uranium-sodium hydroxide-peroxide complex is stable for at least 12 hr, and when ammonium carbonate is used as the alkaline reagent the color is stable at room temperature for at least the same period of time.³⁶⁹ Beer's law is obeyed as shown in Fig. 1.15.¹⁷³ When spectrophotometers with wide band widths are used, there is no deviation from Beer's law up to a band width of 35 m μ .¹⁷² When filter photometers are used there may be some variation from linearity owing to the wide band width employed.¹⁷² This is indicated in Fig. 1.16.

The sensitivity depends chiefly on the instrument used for measurement. A transmittancy of 60 per cent at 325 m μ , using 10-cm

cells with a U_3O_8 concentration of 2γ per milliliter, has been reported.³⁵⁷ With a filter photometer the sensitivity is appreciably lower, as is shown in Fig. 1.16. Visual estimations in the same concentration range have been made by using Nessler tubes. The precision on pure uranium solution is within the experimental error of

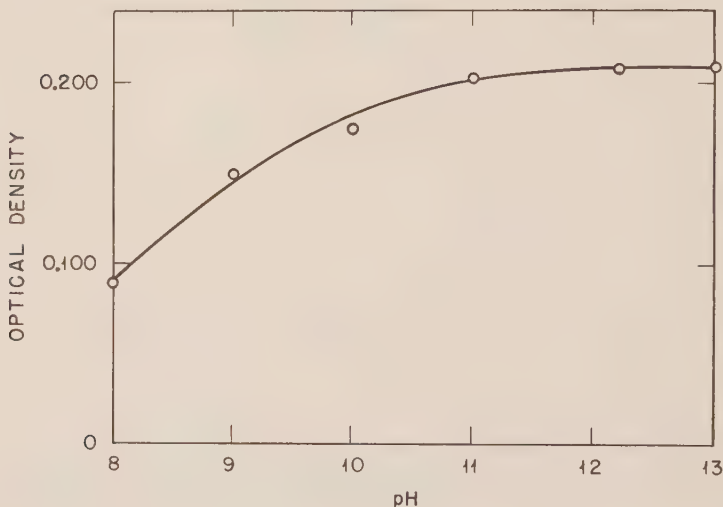


Fig. 1.13—Optical density of an alkaline uranium peroxide solution as a function of pH. Solutions containing 5 mg of uranium, 1 ml of 30 per cent hydrogen peroxide, and 5 ml of 20 per cent sodium carbonate were adjusted to the desired pH by the addition of either 10 per cent sodium hydroxide or dilute sulfuric acid and were diluted to 100 ml. All measurements were made at $400\text{ m}\mu$ against water on the Beckman spectrophotometer using 1-cm cells.

the photometric measurements, which is dependent upon the instrument used.¹⁷³ With the Beckman spectrophotometer the precision is ± 1 per cent.

The effect of acetate, chloride, fluoride, nitrate, phosphate, and sulfate ions has been investigated, and indications are that in the sodium carbonate-peroxide-sodium hydroxide system,¹⁷³ as given in Table 1.4, phosphate and sulfate lead to positive errors. In the sodium hydroxide-peroxide system, chloride, nitrate, and sulfate do not interfere. Phosphate in low concentration does not interfere,^{172, 364} but in high concentration it causes precipitation of sodium phosphate.¹⁷²

In the ammonium hydroxide-peroxide-tartrate system,³⁶⁸ chloride and phosphate interfere, but phosphate has the more serious effect.

(Chloride at 3.5 per cent concentration reduced the optical density 9 per cent, whereas 0.5 per cent phosphate reduced the density 11 per cent.) Up to 12 per cent sulfate had no effect.

Five per cent sodium peroxide or potassium hydroxide-hydrogen peroxide solution has been used to develop the color in the presence

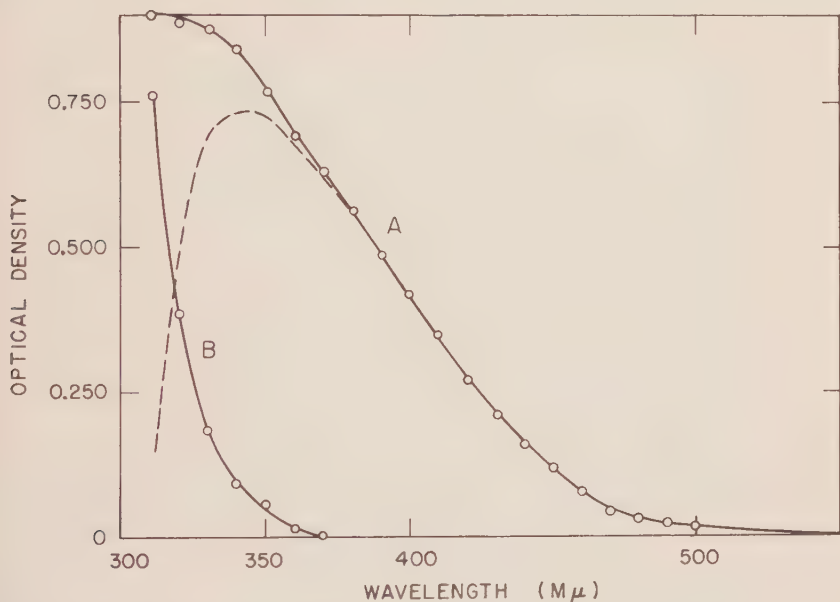


Fig. 1.14—Absorption spectrum of uranium peroxide solution at pH 12. Curve A: A solution of 10 mg of uranium, 1 ml of 30 per cent hydrogen peroxide, and 5 ml of 20 per cent sodium carbonate was prepared and diluted to 100 ml after sufficient 10 per cent sodium hydroxide was added to establish a pH of 12.3. The broken portion indicates the correction for the reagent blank. Curve B: The reagent blank contained all the above reagents except the uranium. All measurements were made against water on the Beckman spectrophotometer using 1-cm cells.

of fluoride ion and salicylic acid. The fluoride ion had little effect, but 6 per cent salicylic acid lowered the transmittancy by 2 to 3 per cent.

The most serious cation interference is caused by chromium, whose spectral absorption overlaps that of the uranium in alkaline peroxide solution as shown in Fig. 1.17.

In all systems employing alkaline peroxide—whether sodium carbonate, sodium hydroxide, or ammonium hydroxide is used as the alkaline medium—chromium offers very serious interference. The correction for chromium by adding known amounts to standards has

not proved satisfactory. The chromium may be removed by oxidation followed by a double ammonium hydroxide precipitation, by ether extraction of the nitrate solution after an ammonium hydroxide precipitation,³⁷⁴ or by electrolysis with a mercury cathode.¹⁷³ The separation of chromium by volatilization as chromyl chloride has been suggested.³⁷⁵

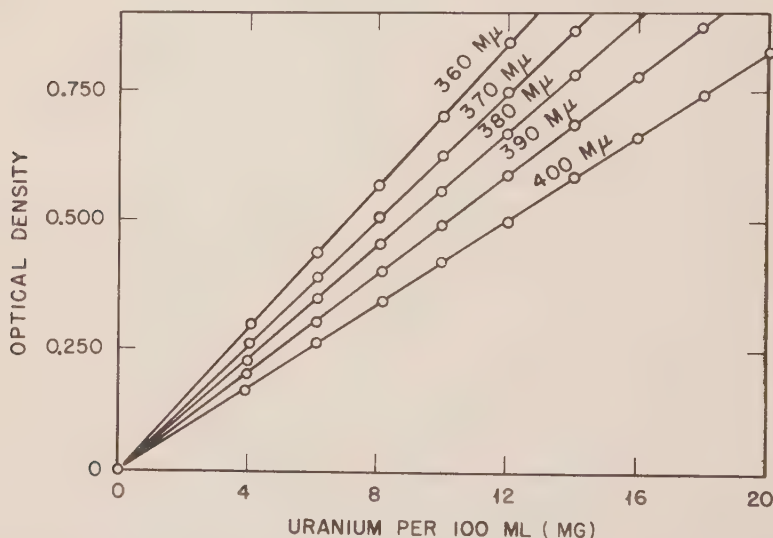


Fig. 1.15—Concentration-optical-density curve of uranium at varying wavelengths. Solutions of uranium, 1 ml of 30 per cent hydrogen peroxide, 5 ml of 20 per cent sodium carbonate, and sufficient sodium hydroxide to establish a pH of 12.5 upon dilution to 100 ml were used. All solutions were measured against water in a Beckman spectrophotometer using 1-cm cells.

Vanadium interferes to a marked extent in the usual procedure and cannot be compensated for by addition of known amounts to standards because the color development with alkaline peroxide is dependent on temperature. When a sodium hydroxide-sodium peroxide system with high alkali content is used and the solution is brought to a boil and then is cooled before photometric measurements are made, the effect of vanadium is eliminated³⁵⁷ as shown in Fig. 1.18. Vanadium cannot be completely separated by ether extraction, and it accompanies uranium to a marked extent in alkaline precipitation separations.

Manganese seriously interferes and gives erratic results. Solutions containing 0 to 5 g of manganese(II), 5 mg of uranium, 5 ml of 20 per cent sodium carbonate, and 5 ml of 10 per cent sodium hydroxide

were boiled, cooled, and filtered after the addition of 1 ml of 30 per cent hydrogen peroxide. The filtrates were diluted to 100 ml, and the absorption was measured at 400 m μ .¹⁷³ The results are shown in Table 1.5.

Occlusion of uranium, apparent adsorption by colloidal manganese dioxide, and catalysis of the peroxide decomposition contributed to the results shown.

Table 1.3—Stability of Hydrogen Peroxide–Sodium Carbonate–Sodium Hydroxide Complex

Concentration of uranium, mg/100 ml	Optical density			
	After 0 hr	After ½ hr	After 2 hr	After 24 hr
0.5	0.025	0.025	0.022	0.022
1.0	0.045	0.045	0.043	0.044
5	0.212	0.213	0.211	0.212
10	0.429	0.426	0.426	0.425

Iron, if present in large amounts, interferes by catalytic decomposition of the peroxide, and it also interferes by adsorption of uranium when separated by filtration. Tartrate has been used to complex iron in the ammonium hydroxide–peroxide–tartrate system.³⁶⁸ Small amounts of iron do not interfere in the sodium hydroxide–sodium peroxide system if the solution is allowed to stand to coagulate the ferric hydroxide before filtration.

Copper and nickel interfere because of their color in the ammonium hydroxide–ammonium carbonate system³⁶⁹ but small amounts do not interfere in the sodium hydroxide–sodium carbonate–peroxide system.¹⁷³ Large amounts give low results, presumably by occlusion of uranium in the hydroxide precipitate. Iron, copper, and nickel may be removed by a sodium carbonate treatment in which the uranium is dissolved. A reprecipitation of the carbonate precipitate, after it is dissolved in acid, may be necessary,³⁶³ but even then in the presence of large amounts of these elements uranium may be retained in the carbonate precipitate.¹⁷²

Molybdenum interferes to some extent, but this interference depends on the peroxide concentration. The interference can be eliminated¹⁷³ by allowing the solution to stand for 2 hr as shown in Table 1.6. The solution contained varying amounts of molybdenum and 30 per cent hydrogen peroxide, as well as 5 ml of 20 per cent Na₂CO₃ and 5 ml of NaOH in a volume of 150 ml.

Interferences by calcium and magnesium have been reported,³⁶⁴ but these elements may be removed by filtration of the alkaline solution. Calcium has been used as a collecting agent for uranium previous to

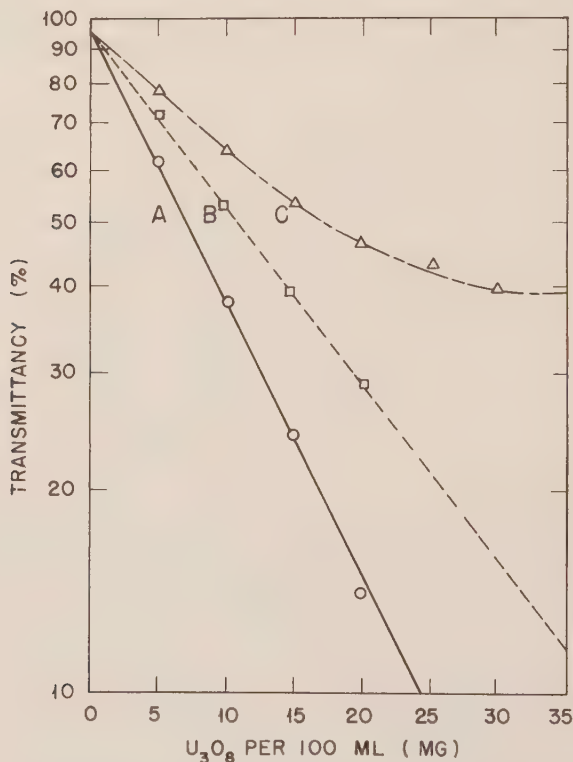


Fig. 1.16—Transmittancies of uranium peroxide solutions with different instruments. Solutions of uranium, 10 ml of sodium hydroxide (1 to 1), and about 1 g of sodium peroxide were diluted to 100 ml. Curve A: A Coleman model 11S spectrophotometer was used, with an additional filter of 2 mm thickness, Corning No. 5113 filter (425-m μ band peak), and 18-mm cylindrical cells. Curve B: A Coleman model 10S spectrophotometer was used, with 425-m μ light source (5-m μ band width) and 18-mm cylindrical cells. Curve C: A Fisher electrophotometer was used, with a Corning No. 5543 filter of 4.16 mm thickness and 25-mm cylindrical cells. All measurements were made against distilled water.

colorimetric determination without interference in the sodium hydroxide-sodium peroxide system.³⁷⁶

The most efficient method for the removal of objectionable interferences is by an ether extraction of the nitrate^{368,374} (see Sec. 2.5 of this chapter). It has been observed¹⁷² that some organic material is

separated by the ether extraction, which gives a color when sodium hydroxide and peroxide are added. It has therefore been found necessary to destroy organic matter after the ether removal by fuming with a mixture of nitric, perchloric, and sulfuric acids.

Table 1.4—Effect of Various Anions on the Determination of 5 Mg of Uranium in Basic Carbonate Medium at pH 12

Anion	Uranium found, mg			
	0 g of anion per liter	10 g of anion per liter	30 g of anion per liter	50 g of anion per liter
Acetate	5.02	4.97	4.88	5.02
Chloride	5.02	5.09	4.90	4.92
Fluoride	5.05	5.05	*	
Nitrate	5.02	4.97	4.92	4.92
Phosphate	5.02	5.16	5.24	5.30
Perchlorate	5.02	5.02	5.00	5.00
Sulfate	5.02	5.05	5.19	5.28

*SiO₂ precipitated.

Another source of interference has been found in certain dilute hydrogen peroxides (3 per cent) that give a yellow color when treated with alkali. This has not been found with the 30 per cent hydrogen peroxide of commerce.

For general use the sodium hydroxide-peroxide system or the sodium hydroxide-sodium carbonate-peroxide system with the transmittancy measured from 400 to 430 m μ is preferred because it is subject to less interference. Conditions are not so critical as in the sodium carbonate-peroxide system. In special cases the ammonium hydroxide-peroxide-tartrate system or the ammonium carbonate-peroxide system is preferred. The two alkaline peroxide procedures described below have been found to be the most satisfactory for general work. The ammonium carbonate-peroxide system has been used occasionally.

Procedure (Sodium Hydroxide-Sodium Peroxide System).¹⁷² The solution, containing 1 to 25 mg of U₃O₈, after being purified by an ether extraction, is evaporated on the steam bath. Two milliliters of H₂SO₄, 3 ml of HNO₃, and 3 ml of HClO₄ are added, and the solution is boiled down in a covered beaker to fumes of SO₃. The beaker is kept in motion to prevent bumping when the volume is low. After it is cooled the beaker is washed down with water, and NaOH solution (1 to 1) is added until the acid is neutralized. About 1 g of Na₂O₂ is added,

and an excess of NaOH solution (1 to 1) amounting to 10 per cent of the final volume is added, and the solution is diluted to the final volume. After filtering through double filter paper (Whatman No. 1) the transmittancy is measured at $425\text{ m}\mu$ against water.

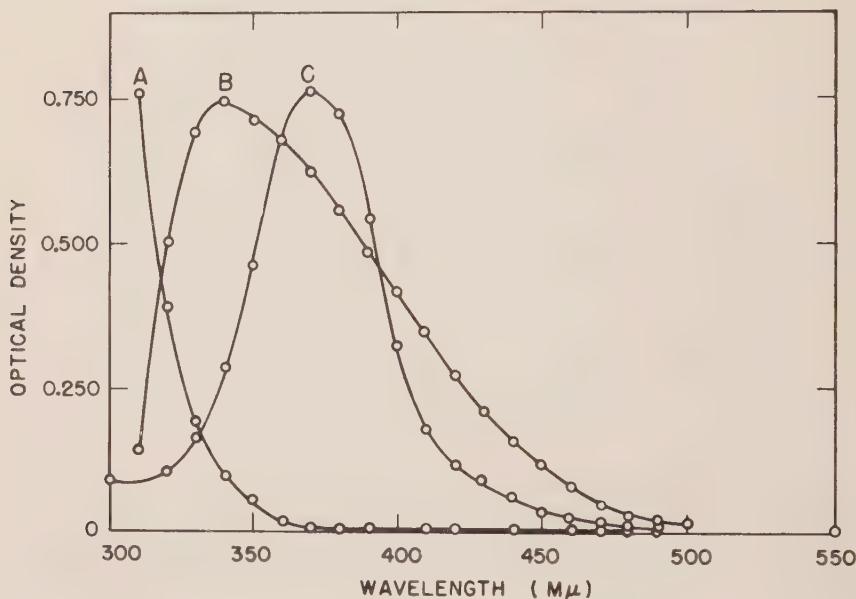


Fig. 1.17—Chromium interference in the alkaline peroxide determination of uranium. Curve A: A solution of 5 ml of 20 per cent sodium carbonate, 5 ml of 10 per cent sodium hydroxide, and 1 ml of 30 per cent hydrogen peroxide was prepared and diluted to 100 ml (pH 12). Curve B: A solution of 10 mg of uranium plus reagents in blank was used. Curve C: A solution of 1 mg of chromium plus reagents in blank was used. Optical densities of uranium and chromium solutions were measured against blank, and optical density of blank was measured against distilled water. All measurements were made with Beckman spectrophotometer using 1-cm cells.

In the presence of vanadium, after the solution is neutralized, 20 ml of NaOH solution (1 to 1) is added, and the volume is made up to 100 ml. Approximately 0.5 g of Na_2O_2 is added, and the solution is filtered through a double Whatman No. 1 filter paper into a 250-ml flask. The flask is covered with a small watch glass, and the solution is brought just to a boil. The solution is allowed to cool, and the transmittancy is measured at $425\text{ m}\mu$ against water. In the event that traces of uranium are to be determined, it is desirable to measure the transmittancy at $370\text{ m}\mu$ against a carefully controlled reagent blank.

Procedure (Sodium Carbonate–Sodium Hydroxide–Hydrogen Peroxide System).¹⁷³ After removal of interfering elements by electrolysis, extraction, or precipitation, the solution is neutralized with 25 per cent sodium hydroxide. Five milliliters of 20 per cent sodium carbonate is added followed by 5 ml of 10 per cent sodium hydroxide.

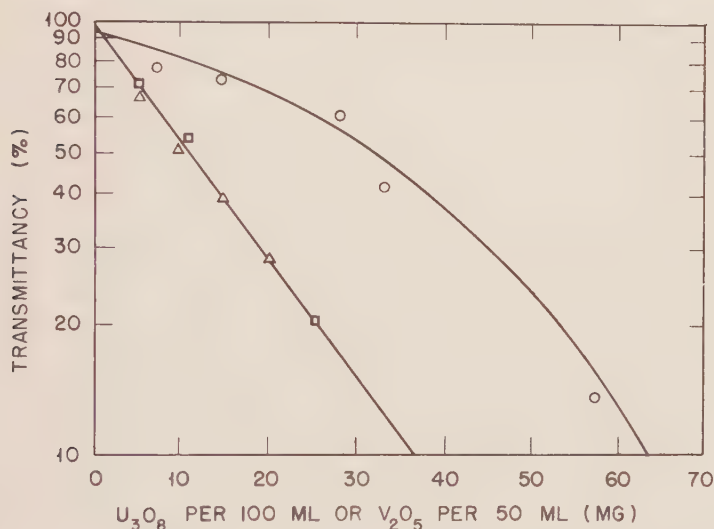


Fig. 1.18—Vanadium interference in the alkaline peroxide determination of uranium. All solutions contained 20 ml of sodium hydroxide (1 to 1) and about 1 g of sodium peroxide diluted to 100 ml. Circled points: vanadium, room temperature; triangular points: uranium, room temperature; squared points: uranium plus 200 mg of V₂O₅ boiled and cooled to room temperature. All measurements were made against water on a Coleman model 10S spectrophotometer using a 425-m μ light source and 5-m μ band width with 18-mm cylindrical cells.

The solution is then boiled and cooled, and after the addition of 1 ml of 30 per cent hydrogen peroxide the solution is filtered and the optical density is measured at 400 m μ .

Procedure (Ammonium Hydroxide–Hydrogen Peroxide–Tartrate System).³⁶⁸ A 50-ml sample containing 2 to 6 mg of uranium is pipetted into a 250-ml separatory funnel. (If large amounts of sulfate or chloride are present an ammonium hydroxide precipitation should be made followed by solution in nitric acid.) The pH is adjusted to 0 or slightly below with nitric acid and 70 g of calcium nitrate is added. The solution is shaken with 50 ml of diethyl ether and allowed to separate, and the water layer is drained into a second separatory funnel.

The water layer is shaken with an additional 45 ml of ether, and, after settling, the aqueous layer is separated and discarded. The ether layers are combined and the second funnel is washed with 5 ml of ether. The combined ether layers are washed with two 1-ml portions of saturated ammonium nitrate in 1N nitric acid, and the wash-

Table 1.5 — Interference by Manganese in the Alkaline Peroxide Determination of Uranium

Mn present, mg	0	4	20	100	1,000	3,000	5,000
U(VI) found, mg	4.95	8.0	4.3	2.6	3.3	0.9	0.14

Table 1.6 — Interference by Molybdenum in the Alkaline Peroxide Determination of Uranium

Mo, mg	H ₂ O ₂ , ml	Optical density				
		Initial	After ½ hr	After 1 hr	After 2 hr	After 4 hr
0	1	0.002	0.002	0.002	0.001	
10	1	0.017	0.010	0.007	0.002	
50	0	0.003	0.003	0.003	0.003	
50	2	0.169	0.037	0.021	0.009	0.005
50	5	0.612	0.164	0.040	0.012	0.004

ings are discarded. (If copper, iron, or chloride content is high, additional back washings may be necessary.) The uranium is washed from the ether with 5 ml of water, 5 ml of 60 per cent ammonium sulfate solution, and two 3-ml portions of water. The wash portions are collected in a 100-ml beaker containing 5 ml of 20 per cent sodium tartrate solution and 15 ml of ammonium hydroxide, and 5 ml of 3 per cent hydrogen peroxide is added. The pH of the solution is adjusted to 9.7 to 9.9 with nitric acid or ammonium hydroxide, if necessary. The solution is transferred to a 50-ml volumetric flask and made up to volume. The transmittancy is then measured in the region of 400 to 500 m μ . The standardization curve is prepared with known uranium concentrations and with the above concentration of other salts.

(3) Acid Peroxide Method. The use of an acid medium for the peroxide colorimetric determination has been developed.^{173, 370, 371}

The absorption spectrum of uranium peroxide varies greatly with the pH. Figure 1.19 indicates this variation. A plateau from pH 4 to

pH 5.5, however, indicates that close pH control is not necessary and the required pH can be readily attained with an acetate buffer. The spectral transmittancy of uranium peroxide at pH 4.5 is given in Fig. 1.20. There is no region in which the absorption is independent of wavelength. Any wavelength from 330 to 400 $m\mu$ can be used,

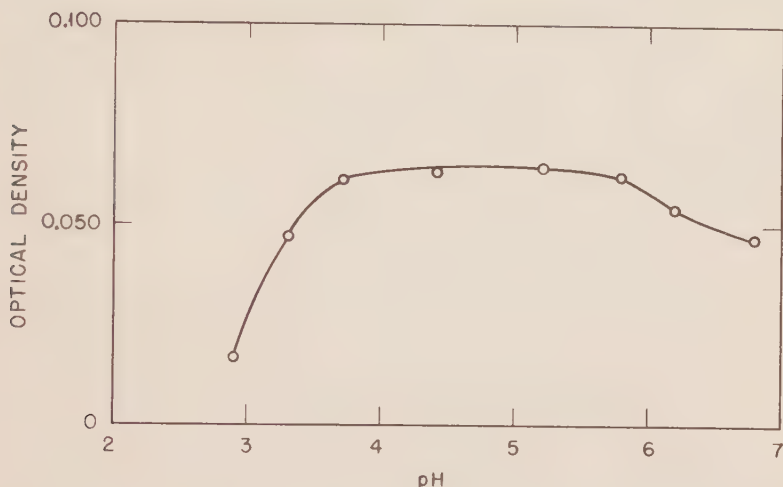


Fig. 1.19—Optical density of an acid uranium peroxide solution as a function of pH. Solutions of 5 mg of uranium, 1 ml of 30 per cent hydrogen peroxide, and 5 ml of 20 per cent sodium carbonate were adjusted to the desired pH by the addition of dilute sulfuric acid and were diluted to 100 ml. All solutions were measured at 400 $m\mu$ against water on the Beckman spectrophotometer using 1-cm cells.

although the sensitivity is greater in the lower wavelengths. A wavelength of 350 $m\mu$ was finally selected, chiefly because certain interferences were not so objectionable at this wavelength.

The effect of peroxide concentration on the absorption at 350 $m\mu$ was investigated. Solutions were prepared containing 5 mg of uranium, 10 ml of acetate buffer (1M in sodium acetate and acetic acid with pH 4.5), and varying amounts of 30 per cent H_2O_2 and diluted to 100 ml. The effect of varying the peroxide concentration (from 1 to 20 ml) on the absorption at 350 $m\mu$ was a variation in the optical density from 0.003 to 0.046. However, the amount of peroxide used is not critical as long as a blank containing a similar amount of peroxide is used. The standard amount of peroxide that is recommended is 1 ml of 30 per cent H_2O_2 per 100 ml of solution.

The stability of uranium peroxide in acid mediums was investigated. Solutions containing various amounts of uranium were prepared to

conform to the standard conditions adopted, that is, to contain 1 ml of 30 per cent hydrogen peroxide and 10 ml of pH 4.5 acetate buffer. After dilution to 100 ml the optical density at 350 $m\mu$ of each of these solutions was measured at various times for a period of 3 hr to determine their stability with the results obtained as shown in Table 1.7.

The data show that the stability of uranium peroxide in acid mediums is limited by the fact that uranium peroxide finally precipitates.

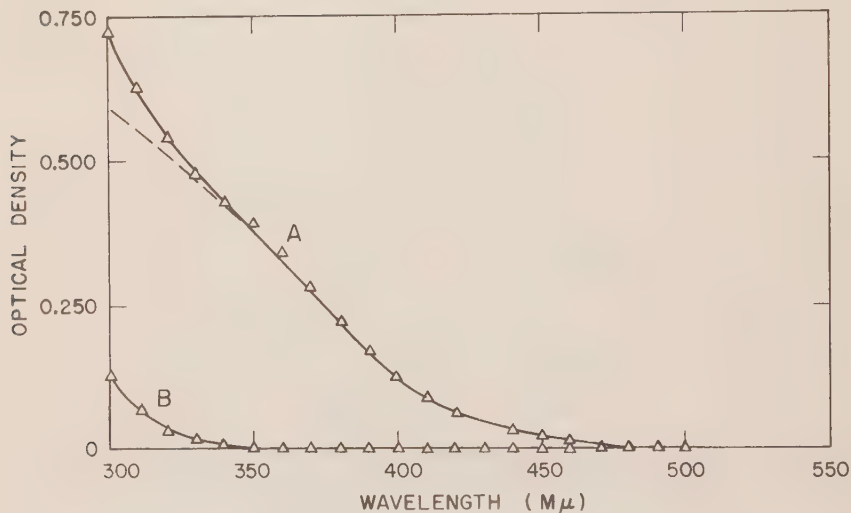


Fig. 1.20 — Optical density of an acid uranium peroxide solution as a function of wavelength. Curve A: A solution of 10 mg of uranium, 1 ml of 30 per cent hydrogen peroxide, and 10 ml of a buffer (equal amounts of 1M sodium acetate and 1M acetic acid) in a volume of 100 ml (pH 4.5) was measured against water with a Beckman spectrophotometer using a 1-cm cell. Curve B: The reagent blank contained all the above except the uranium; the blank was measured against water. Curve C: This curve indicates the correction for the reagent blank.

This precipitation is influenced by a number of factors and is much more rapid with large amounts of uranium. On the other hand, the presence of sulfate³⁶⁸ tends to hold the uranium peroxide in solution for much longer periods of time.

Beer's law is followed at all wavelengths tested. When a 1-cm cell in the Beckman spectrophotometer is used, the limiting sensitivity at 350 $m\mu$ is about 10 mg of uranium per liter. The precision obtained on pure uranium solutions with this instrument is ± 1 per cent.

The effect of various anions is shown in Table 1.8. Little interference is caused by the anions in question when present in small

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amounts (1 g per 100 ml), but in larger amounts there is a slight positive error even if blanks containing the same amounts of anion are employed. Sulfates tend to retard the precipitation of uranium

Table 1.7—Stability of the Peroxide Complex in Acid Mediums

Concentration of uranium, mg/100 ml	Optical density					
	After 0 hr	After ¼ hr	After ½ hr	After 1 hr	After 2 hr	After 3 hr
0	0.001	0.001	0.001	0.002	0.001	0.001
4	0.155	0.155	0.155	0.157	0.156	0.156
8	0.314	0.313	0.314	0.317	*	
12	0.472	0.472	0.472	0.480	*	
16	0.630	0.630	0.631	*		
20	0.790	0.795	*			

* Uranium peroxide began to precipitate.

Table 1.8—Effect of Various Anions on the Determination of Uranium at pH 4.5

Anion	Amount, g	Optical density at 350 m μ		
		Blank	With peroxide	Corrected
Chloride	0	0.000	0.195	0.195
	1	0.001	0.199	0.198
	3	0.001	0.197	0.196
	5	0.001	0.202	0.201
Nitrate	0	0.000	0.195	0.195
	1	0.000	0.199	0.199
	3	0.007	0.208	0.201
	5	0.010	0.215	0.205
Sulfate	0	0.000	0.195	0.195
	1	0.001	0.201	0.200
	3	0.009	0.209	0.200
	5	0.014	0.216	0.202

peroxide. If 1 g of sodium sulfate is added to the solution shown in Table 1.7, no precipitate is formed except after 5 hr with 16 and 20 mg of uranium. Addition of sodium or ammonium sulfate is advisable if large amounts (more than 100 mg per liter) of uranium are to be determined.

Chromium, manganese, copper, zinc, cadmium, lead, nickel, and aluminum show very little interference in concentrations up to 50 mg

per 100 ml. Since some of these elements show more interference in alkaline peroxide solution the acid peroxide method has very definite advantage in certain cases. Iron seriously interferes even though peroxide has no effect on the absorption of the iron cation, because at the wavelengths at which uranium peroxide in acid medium is measured the absorption of the iron cation is very large, as is shown in Fig. 1.21. For amounts of iron less than 0.5 mg per 100 ml the effect can be corrected for by taking a reading prior to the addition of peroxide.

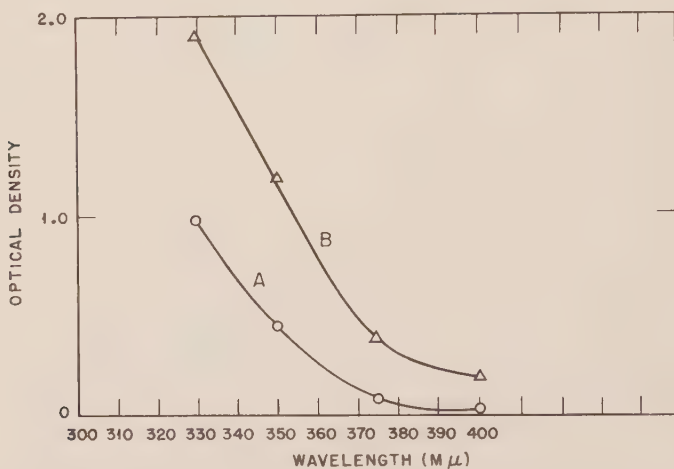


Fig. 1.21—Iron interference in colorimetric uranium peroxide determination. Curve A, 10 mg of iron(III) per 100 ml as the sulfate, pH 1.3; curve B, 10 mg of iron(III) per 100 ml as the nitrate, pH 2.7. Optical densities were measured against water with the Beckman spectrophotometer using 1-cm cell.

Hydrogen peroxide when added to molybdenum in acid solution causes a pronounced absorption as shown in Fig. 1.22, but there is no change in optical density with pH change. It is therefore advisable to remove the molybdenum before determination of the uranium.

Interfering elements may be removed by mercury-cathode electrolysis and by ether extraction of the nitrate. (In the presence of silica the separation of molybdenum is not successful.) Iron may be removed by ammonium carbonate separation.

Procedure. A 1-ml sample is added to 10 ml of saturated ammonium nitrate solution (1N in nitric acid) and extracted with ether (cf. Sec. 2.5 of this chapter). The uranium is extracted from the ether layer with a 15-ml portion of three-fourths saturated ammonium

sulfate. After it is filtered, the solution is treated with 10 ml of acetate buffer, which consists of equal portions of 1M sodium acetate and 1M acetic acid, and brought to a pH of 4.5 with ammonium hydroxide. After 1 ml of 30 per cent hydrogen peroxide is added the solution is diluted to either 50 or 100 ml, and the optical density is measured at 350 $m\mu$. The uranium content is then obtained from a standard curve.

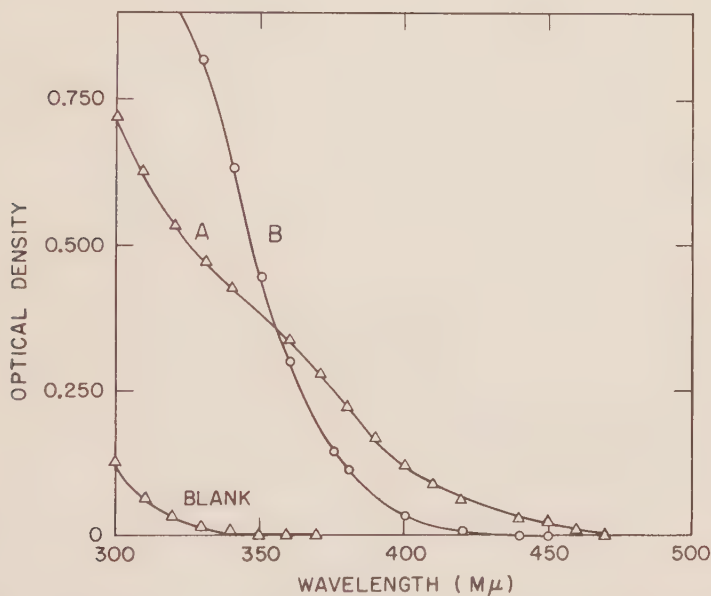


Fig. 1.22—Interference of molybdenum in the acid-peroxide method. Curve A: A solution of 10 mg of uranium, 1 ml of 30 per cent hydrogen peroxide, and 10 ml of a buffer (equal amounts of 1M sodium acetate and 1M acetic acid) was prepared in a volume of 100 ml (pH 4.5) and was measured against water with a Beckman spectrophotometer using 1-cm cells. Curve B: Ten milligrams of molybdenum as ammonium molybdate was treated in the same manner as the uranium. Blank: Optical densities of a solution of all the above except the uranium or molybdenum were measured against water.

(4) Determination with Ferrocyanide. In dilute acid solutions uranium(VI) forms with ferrocyanide a reddish-brown color that can be used for its colorimetric determination. Smales and Wilson^{71,377} developed the color in dilute sulfuric acid solution. Cohenour, Weil, and Stokinger³⁷⁸ have reported a method, which is based on the work of Tissier and Bernard,³⁷⁹ in which 0.056N acetic acid is used. Muntz³⁸⁰ also used acetic acid in a similar method. A sodium formate-formic

acid buffer has been used to control the pH.³⁸¹ Some investigators have added sulfite to their ferrocyanide reagent to improve its stability, but this does not seem to be essential. Gum arabic has been used in some cases to improve the colloidal character of the suspension.

The production of the color is dependent on the pH of the solution, the concentration of potassium ferrocyanide, and the time allowed for development.³⁸¹ Of these three factors the pH is the most critical. In a basic solution the uranyl ferrocyanide color does not form, and the uranyl ion is precipitated. (The ferrocyanide ion has no inhibiting action on this precipitation.) As a solution of uranyl and ferrocyanide ions is acidified the color intensity passes through a maximum and then fades to a very light yellow at a pH of about 1. It was found that the most intense color was produced between a pH of 4 and 6; therefore, a pH of 5 was chosen as the optimum value. Several buffer systems were tried before formate was finally chosen. All the other buffers that were tried, such as acetate, tartrate, citrate, and others, had a bleaching action on the color.

The amount of ferrocyanide added to the uranyl solution has a pronounced effect upon the color intensity. As a general rule, it may be said that the more ferrocyanide that is added, the deeper the color that will be produced. It was found that about 25 ml of 10 per cent ferrocyanide was enough to produce almost the maximum color in 100 ml of solution, because the rate of increase of color with more reagent became very low after this point was passed.

Below 0.5 mg of uranium per 100 ml, the change of color with time was eliminated by the use of the formate buffer. Solutions in this range of concentrations prepared with formate buffer will stand up to 24 hr without change in color. Above 0.5 mg of uranium per 100 ml, it was found that the solution became darker upon standing. Up to a concentration of 1.1 mg of uranium per 100 ml, there is very little change in color for the first 15 min after preparation; therefore, it is recommended that the transmittancy be read within this period.

Templeton³⁸² has shown that in nitric acid solution the acidity must be less than 0.1N, but in the range 0.01N to 0.1N the color is not very dependent on the acidity. Absorption spectra for the complex in such solutions are shown in Fig. 1.23. At 480 m μ the absorption follows Beer's law with good precision for the range 8 to 40 γ per milliliter (Fig. 1.24). At lower wavelengths the data are erratic and deviate considerably from Beer's law, and the reagents begin to absorb light appreciably. For nitric acid concentrations of approximately 1N the red-brown color is not formed, and the yellow solution is very transparent down to about 480 m μ . Below 450 m μ the solution is very opaque, but the dependence of this color on uranium concentration has not been investigated.

In nitric acid solutions that contain less than 6 γ of uranium per milliliter, Beer's law is not obeyed (Fig. 1.24), and the color is yellow rather than red. Cohenour, Weil, and Stokinger³⁷⁸ reported similar behavior in acetic acid solution. This effect was not observed when the formate buffer method of Lafferty et al.³⁸¹ was used, as shown in Fig. 1.25.

Ammonium acetate has been found to inhibit color development, and high concentrations of other salts may have the same effect. Metallic

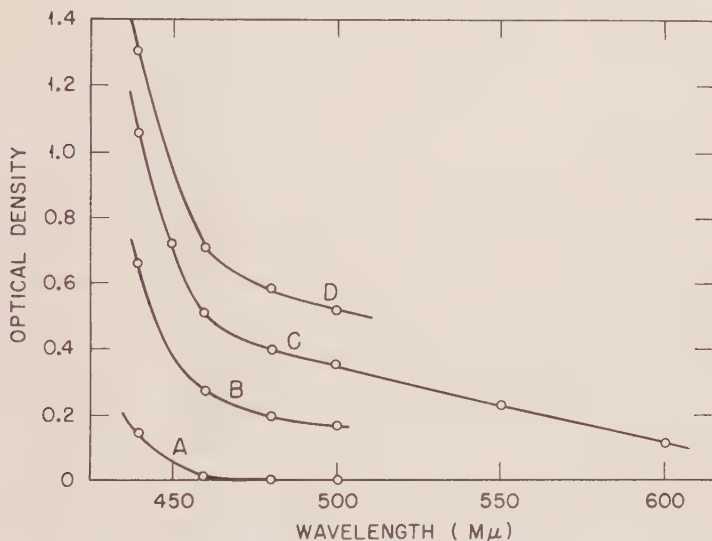


Fig. 1.23—Optical density of uranyl ferrocyanide in 0.05N nitric acid solution. The solutions were measured against water with a Beckman spectrophotometer using 1-cm cells. Curve A, blank; curve B, 300 γ per 25 ml; curve C, 600 γ per 25 ml; curve D, 900 γ per 25 ml.

ions that form colored or insoluble compounds with the ferrocyanide ion produce a positive interference. The principal ions in this group are ferric, cupric, and nickelous. Fluoride ion in a molar ratio of fluoride ion to uranyl ion greater than 3 to 1 produces a negative interference. This interference is eliminated by evaporation to dryness with sulfuric acid. Sulfate ion interferes if the molar ratio of sulfate ion to uranyl ion is greater than 100 to 1. Evaporating completely to dryness with sulfuric acid leaves the ratio 1 to 1 unless metallic ions other than uranyl are present. If such metallic ions are present in sufficient amount, the fluoride interference cannot be eliminated by this method. Anions such as tartrate, citrate, acetate, and carbonate, which form complexes with uranyl ion, bleach the

color. These are also removed by the evaporation to dryness with sulfuric acid. It should be noted that tartrate and citrate ions are difficult to decompose with the usual fuming with sulfuric acid.

Procedure (Using Nitric Acid).³⁸² A sample of 0.2 to 1.0 mg of uranium, and no other metal ion, in mineral acid solution is placed in

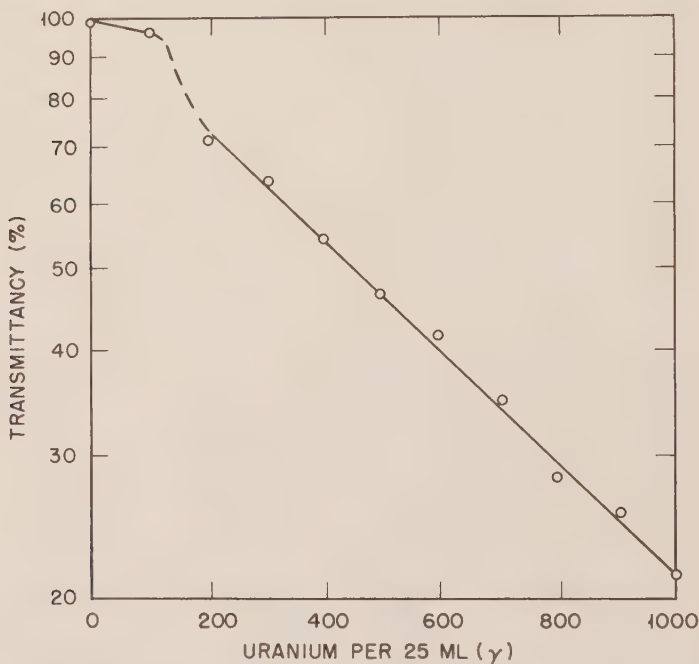


Fig. 1.24—Standard curve for the determination of uranium with ferrocyanide using HNO_3 . Solutions were prepared as described in text. All measurements were made against distilled water on Beckman spectrophotometer at $480 \text{ m}\mu$ using 1.0-cm cells.

a 25-ml volumetric flask and diluted to approximately 15 ml. One drop of phenolphthalein indicator is added, and the solution is neutralized with ammonium hydroxide, which is added drop by drop until the first pink color appears. Three drops of nitric acid are then added; the color should change with the first drop. One milliliter of 3 per cent potassium ferrocyanide is added, and the solution is diluted to 25 ml, mixed well, and allowed to stand a few minutes. The transmittancy is measured at $480 \text{ m}\mu$ with a spectrophotometer, using 1-cm cells and with distilled water as a reference.

Procedure (Using Sodium Formate).³⁸¹ This procedure eliminates the interference of anions of fluoride, sulfate, acetate, citrate, tar-

trate, and carbonate. A volume of solution that contains 0.05 to 1.1 mg of uranium is pipetted into a clean 100-ml beaker and evaporated to dryness without boiling. After it is cooled, 0.5 ml of dilute sulfuric acid (1 to 6) is added, and the solution is evaporated until no more fuming occurs. The sample is cooled and taken up with distilled

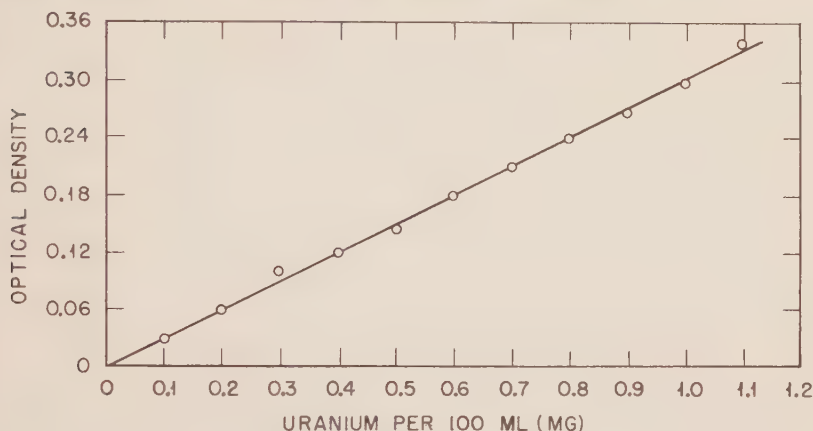


Fig. 1.25—Standard curve for the determination of uranium with ferrocyanide using formate buffer. Solutions of uranium, 10 ml of buffer, and 25 ml of potassium ferrocyanide reagent were diluted to 100 ml, and optical densities were measured on a Beckman spectrophotometer at 525 $m\mu$ using 1-cm cells.

water. The sides of the beaker and the watch glass are washed down by using no more than 30 ml of water. A few drops of sulfuric acid are added, and the sample is heated for 10 min. Ten milliliters of buffer solution (made by dissolving 68 g of sodium formate in 500 ml of H_2O , adding 2 ml of formic acid, stirring the solution, and adjusting the pH to 5.0 with sodium formate or formic acid) is added to the solution. The pH of the solution should be 5.0 ± 0.2 at this point. If it is more acid, adjustment should be made with NH_4OH (1 to 6). The solution is then filtered into a 100-ml volumetric flask. The beaker and paper are washed thoroughly. The volume of the solution in the flask should not be more than 65 ml at this point. Exactly 25 ml of 10 per cent potassium ferrocyanide solution is added, and the flask is filled to the mark with distilled water. A blank is prepared by diluting 25 ml of potassium ferrocyanide solution and 10 ml of the buffer solution to 100 ml in a volumetric flask. The transmittancy of the solution is determined against the blank with a filter photometer using a Corning No. 4010 filter. The transmittancy should be read within 15 min. The concentration of uranium in the solution is determined

from a calibration curve made from known amounts of uranium. This curve should be constructed for each new lot of ferrocyanide.

(5) Determination with Thiocyanate. A method for the colorimetric determination of uranium by using ammonium thiocyanate was the subject of two reports.^{383,384} Thiocyanate ion reacts with uranyl ion in acid solution to form a yellow-colored complex.³⁸⁵ Spectral transmittancy of this complex (Fig. 1.26) is somewhat similar to those of the peroxide and ferrocyanide. The absorption increases rapidly with decreasing wavelength below $400\text{ m}\mu$. The reagents used absorb strongly below $360\text{ m}\mu$. The method is particularly useful in the presence of iron, which is reduced to the ferrous condition with stannous chloride, and its sensitivity compares favorably with other methods. In one method using 2-cm cells and a wavelength of $365\text{ m}\mu$ amounts of uranium in the range of 0.05 to 0.7 mg of uranium per 25 ml can be analyzed satisfactorily. An accuracy of 2 per cent is claimed.

The pH must be kept within the range 0.2 to 1.0, as is shown in Fig. 1.27. The amount of reagent that is added and the interval between addition of thiocyanate and reading of transmittancy must be carefully controlled. Beer's law is not obeyed (Fig. 1.28) by using the procedure given below in which a Beckman spectrophotometer with approximately $1\text{-m}\mu$ band width was employed. By using a standard curve, however, reproducible results may be obtained. When measurements were made with a filter photometer at $365\text{ m}\mu$ ³⁸³ or with a Coleman model 11S wide-band spectrophotometer³⁸⁴ the divergence from Beer's law was negligible.

Molybdenum and ruthenium interfere seriously. More than small amounts of lead interfere, but lead may be removed by precipitating and filtering off the sulfate. Not much sulfate may be tolerated. No appreciable interference was found when 1-mg amounts of thorium, barium, tin, cerium, lanthanum, yttrium, zirconium, beryllium, iron, tellurium, bromide, iodide, and iodate were added. Carbonates do not interfere, but organic matter and more than small amounts of peroxide must be destroyed. The method³⁸⁴ described below has been found to be particularly useful for the analysis of uranium in thorium samples.

Procedure.³⁸⁴ An aliquot of the sample is pipetted into a 25-ml volumetric flask, and the pH is adjusted to between 0.2 and 1.0 with 1N HCl or 1N KOH. Two milliliters of 10 per cent SnCl_2 (50 g of SnCl_2 plus 50 ml of HCl diluted to 500 ml) is added and the mixture is thoroughly shaken. Ten milliliters of 8M ammonium thiocyanate is then added; the solution is again thoroughly shaken and is made up to volume. The transmittancy is read immediately at $360\text{ m}\mu$ against a blank made up with 1 ml of 1N HCl plus the added reagents.

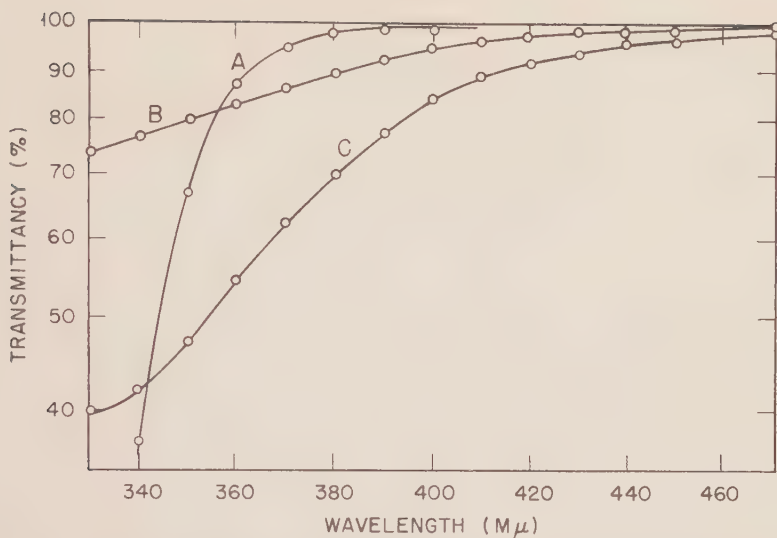


Fig. 1.26 —Spectral transmittancy of uranyl thiocyanate. Solutions were prepared and transmittancies were measured as described under procedure in text. Curve A, blank against distilled water; curve B, 100 γ of uranium against blank; curve C, 300 γ of uranium against blank.

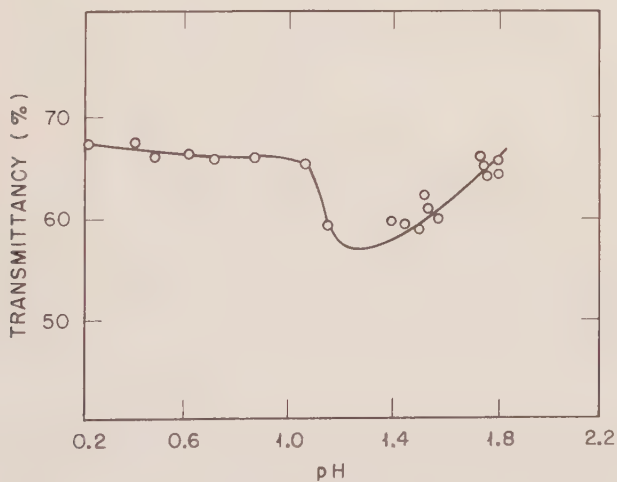


Fig. 1.27 —Effect of pH on the transmittancy of the uranyl thiocyanate system. Solutions were prepared at different pH's and treated as described under procedure in text.

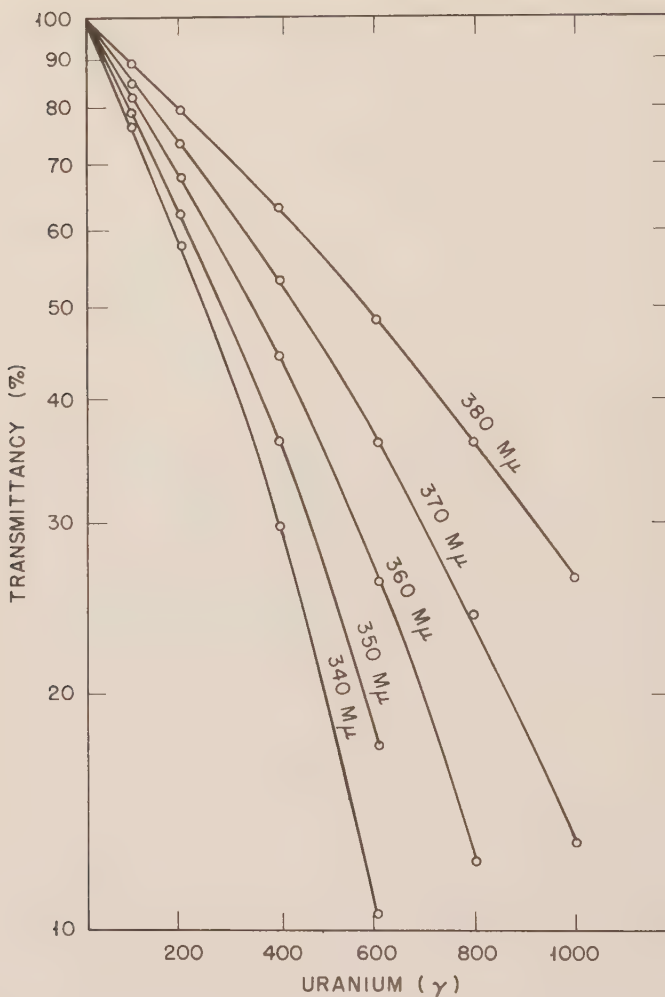


Fig. 1.28 — Transmittancy-concentration curves of uranyl thiocyanate at various wavelengths. Solution was prepared as in text, and measurements were made with a Beckman spectrophotometer.

(c) Organic Compounds or Complexes of Uranium. Many organic reagents have been suggested for the colorimetric analysis of uranium. The published literature has been surveyed by E. Ware.⁴² A representative list of reagents that have been suggested is given in Table 1.9.

More complete lists of organic reagents for uranium are given elsewhere.^{42, 388, 394 a} Many of these reagents can be used for pure uranium solutions only, and therefore a complete separation is necessary before analysis. The principal organic reagents investigated were *l*-ascorbic acid (see references 371, 389, and 394-399), cacothe-line,^{395, 400} chromotropic acid,³⁹¹ cresotates,³⁹³ diethyl dithiocarbamate (see references 401-406), 8-hydroxyquinoline (see references 53, 71, 407-411), salicylates (see references 395 and 412-416), and alizarin red S.⁴¹⁷

(1) Determination by *l*-Ascorbic Acid. Ascorbic acid was reported by Emmerie⁴¹⁸ to give a reddish-brown color with uranyl acetate solution. Extensive investigations of its application (see references 371, 389, and 394-399) have found the color to be stable and to suffer less from the usual interfering ions such as iron(III), chromium(III), and lead(II). The interference of copper was eliminated by complexing it with pyridine.³⁹⁶

Although the spectral transmittancy curve has not been reported, transmittancy measurements have been made at wavelengths of 335 (see reference 394) and 400 $m\mu$ ³⁸⁹ without the use of pyridine and at 410 and 440 $m\mu$ ³⁹⁶ with the use of pyridine. Beer's law was obeyed in all cases when monochromatic light was used.

The effect of pH in the absence of pyridine is shown in Fig. 1.29. It was noted that the color produced in strongly basic medium was more intense than that in acidic medium. However, the color was found to be unstable in the alkaline medium. The optimum condition appeared to be in a limited range about pH 4.6. The effect of pH after the addition of pyridine is also shown in Fig. 1.29. The color produced is independent of pH between pH 4.3 and 4.8.

The ascorbic acid concentration has an effect on the color. The concentration of the acetate buffer used was found to affect the color intensity. The buffer-ascorbic acid ratio effect is shown in Fig. 1.30. In the case where no buffer was employed the color was more intense but not stable. The presence of even 1 ml of the prepared buffer stabilized the color for several hours.

The effect of various ions using the pyridine system is given in Table 1.10, which has been composited from several reports (see references 371, 396-398, 402, 419, and 420). Although the interferences have not been critically studied the values that are given indicate the magnitude of the interferences. However, although the color obtained with *l*-ascorbic acid is affected less by impurities than that obtained with many of the other organic reagents employed in the determination of uranium, a preliminary separation such as a diethyl

Table 1.9—Organic Reagents for the Colorimetric Determination of Uranium

Reagent	Type of reaction*	Conditions	Interferences	References
Acridine	P, yellow	NaCNS	Bi, Cd, Co, Cu(II), Fe(III), Hg(II), Zn	42, 386
Alizarin Alizarin red S	C, blue	Neutral or slightly acid	Numerous cations	42, 387, 388
Aluminon	C, red	CH ₃ COONa buffer	B, F, and numerous cations, especially Al	42, 387, 388
Ammonium dithiocarbamate	C, yellow	CH ₃ COOH Neutral or slightly alkaline	Cu(II), Fe(III), Ni, Pb, Sn(II), Ag, Al, Bi, Co, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Zn	42, 388
Anthranilic acid	P		Cd, Co, Cu, Hg(II), Mn, Ni, Pb, Zn	387
Aliphatic amines	P C, yellow to light orange		Numerous cations	42, 388
Anthraquinone-1-azo-4-dimethyl aniline hydrochloride	C, red violet		Al, Au, Cd, Ga, Hg(II), Ir, Mo, Pt, Sb, Sn(IV), Zn	42
Antipyrine Pyrimidon Quinaldine <i>p</i> -Nitroso-dimethyl aniline Acetanilide Phenacetin Exalgin	P	Water or alcohol solution	Bi, Co, Fe, Hg, NO ₂ , Sb, Sn, Ti, W	42, 386, 387
Arsanilic (<i>p</i> -aminobenzene-arsonic) acid	P, red	Acetate	Ce, SO ₄ , Zr	42, 387
Ascorbic acid	C, yellow	CH ₃ COONH ₄ buffer and pyridine	Numerous cations; NO ₃ , PO ₄ , SO ₄ , F, citrate, oxalate, tartrate	42, 389
Benzopurpurin 4B	C, brown-red		Al, Ag, Hg(I), Hg(II)	42
Bromphenol blue	C, red-brown		Ag, Cu(II), Hg(I), Hg(II), Pb	42
α -Benzoinoxime	P, yellow	Acid medium	Cb, Cr, Cu, Fe, Mo, Ni, Pd, Ta, V, W	386, 390
Cacotheline	C, violet	SnCl ₂	Cb, Cr, Mo, Rh, Ti, V	42, 387
Carminic acid (cochineal)	C, green		Al, Pb, Zr	42, 388
Chromotropic (1,8-dihydroxy-naphthalene-3,6-disulfonic) acid	C, amethyst	Acidic sulfite	Ag, Co, Cr, Fe, Hg, Mn, Ti, Zr, CO ₃ , PO ₄	42, 387, 391
Hydroquinone Pyrogallol Pyrocatechin Catechol Resorcinol Cresol Phloroglucinol Eugenol Naphthol Guaiacol	C	Neutral pyridine	Fe(II) and many other cations, NO ₃	42, 387
Cupferron	P, yellow	Neutral	Many cations (alkali metals do not interfere)	42, 388
Diethyl dithiocarbamate	P, yellow	Neutral	Bi, Cd, Co, Cu, Fe, Hg, Mn, Ni	42, 387, 392

Table 1.9 — (Continued)

Reagent	Type of reaction*	Conditions	Interferences	References
1,4-dihydroxyanthra-quinone	P, lake	Acetate or formate	Ce, Co, Cu(II), La, Y, rare earths	42
Dihydroxymaleic acid Dihydroxytartaric acid	C, red-brown	Neutral	Mo, Ti, F, acids	42, 386
1,2-Dihydroxynaphthalene	P, red	Pyridine		42
Diphenylthiocarbazide	C, yellow P, yellow C, Orange	CH ₃ COOH Neutral Alkaline	Ag, Bi, Cd, Co, Cu, Fe, Hg, Ni, Pb	42, 387, 388
Gallic acid Tannic acid	C, brown	CH ₃ COONa	Many cations, acids	42, 386 387, 388
Gentisic acid o-Hydroxycoumaric acid Hydroxynaphthoic acid Protocatechuic acid Pyrogallol carboxylic acid Quinic acid Resorcylic acid Salicylic acid	C, red to brown	Neutral	Many cations, acids	42, 388
1-Hydroxyanthraquinone	P, purple-brown C, purple	Methanol	Co, Cu(II), Hf, Mg, Mn, Ni, Zr	42, 387
8-Hydroxyquinoline	P, red-brown C, yellow-brown	Weakly acidic Weakly acidic CHCl ₃	Many cations	42, 388
Isatin-β-oxime	P, red to yellow	Weakly acid CH ₃ COONa	Hg(II) Ag, Co, Cu(II), Fe(II), Hg, Ni, Pb	42
Isojuglone	P, red	Neutral	Cd, Co, Cu(II), Fe, Hg, Ni, Pb, Zn	42
Morphine	C, red to brown P, red to yellow	Neutral	Ce, Cu, Th, Ti, Tl, rare earths	42
α-Nitroso-β-naphthol	P, yellow C	Neutral or slightly acid with CH ₃ COOH	B, Co, Cu, Fe, Mo, Pd, V, Zr	42, 387
Phenanthrene quinone-monoxime Chrysene quinone-monoxime	P, yellow P, yellow to orange	Ethanol	Cd, Cr, Cu, Hg(I), Pb, Pd, Rh, Zn, Mn	42
Phthiocal	P, red to brown	Methanol, neutral	Co, Cu(II), Fe, Mg, Mn, Zn	42
Potassium ethyl xanthate	C, yellow-brown		Many cations	42
Quercetin Morin	C, rust-red	Neutral	Al, Fe(III), Ga, In, Sc Acids	42, 387
Quinaldic acid	P, yellow	Neutral or weakly acidic	Cd, Cr, Cu(II), Al, Fe, Zn, Ti	42, 386
Rhodizonic acid	P, brown	Neutral	Ba, Cu(II), Fe, Pb, Sn, Zn	42, 386, 387
Thioglycolic acid	P, orange-yellow		Ag, Au, Bi, Cu, Co, Fe, Hg(I), Mn, Mo, Ni, Pb, Sn(II), W	42, 386
Turmeric	C, brown C, violet-black	Neutral Na ₂ CO ₃	Al, B, Be, Cb, F, Fe, I, Mg, Mo, PO ₄ , Ta, Ti, W, Zr	386, 388
Sodium cresotate	C, yellow	Alkaline	Cu, Fe	393

*C indicates color, and P indicates precipitate.

ether extraction of the nitrate is necessary. The adverse effect of common anions such as sulfate, fluoride, and phosphate makes this reagent less applicable than some of the other reagents. The reagent can be used for control work when it is applied to material containing known impurities.

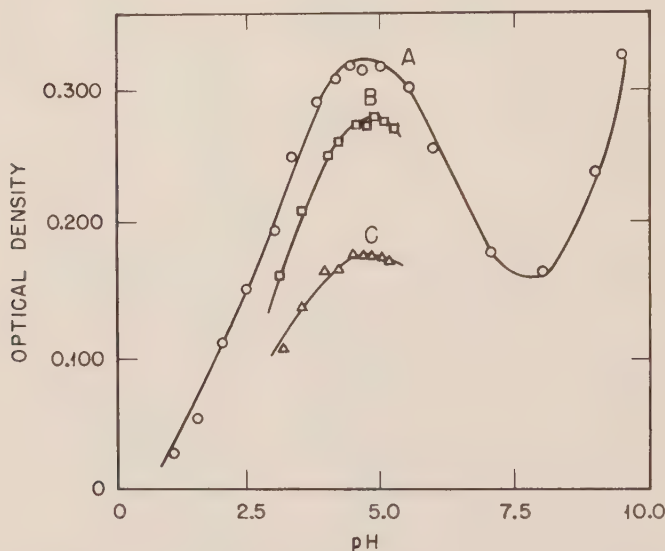


Fig. 1.29—Effect of pH on the optical density of the *l*-ascorbic acid system. Curve A: Solutions of 2 mg of uranium as the nitrate in 10 ml of water were treated with 8 ml of buffer solution (160 ml of 1N ammonium acetate solution, 10 ml of 5N acetic acid solution, and 180 ml of water) and 10 ml of 12 per cent ascorbic acid solution, and the pH was adjusted to the desired value by the addition of ammonium hydroxide or hydrochloric acid. The solutions were made up to 50 ml, and the optical densities were measured against water at 400 m μ . Curve B: Solutions were prepared as for curve A, except that 2 ml of a 10 per cent pyridine solution was added before the addition of ascorbic acid, and the optical densities were measured against water at 410 m μ . Curve C: Solutions were prepared as for curve B, except that optical densities were measured against water at 440 m μ . All measurements were made with the Beckman spectrophotometer using 1-cm cells.

Procedure (After Diethyl Ether Extraction).³⁹⁶ The ether layer is evaporated over 10 ml of water, and the aqueous layer is treated with 8 ml of buffer (160 ml of 1N ammonium acetate, 10 ml of 5N acetic acid, and 180 ml of water) followed by 2 ml of 10 per cent pyridine solution and 10 ml of 12 per cent *l*-ascorbic acid. The pH is adjusted to 4.6 ± 0.1 with ammonium hydroxide or hydrochloric acid, and the

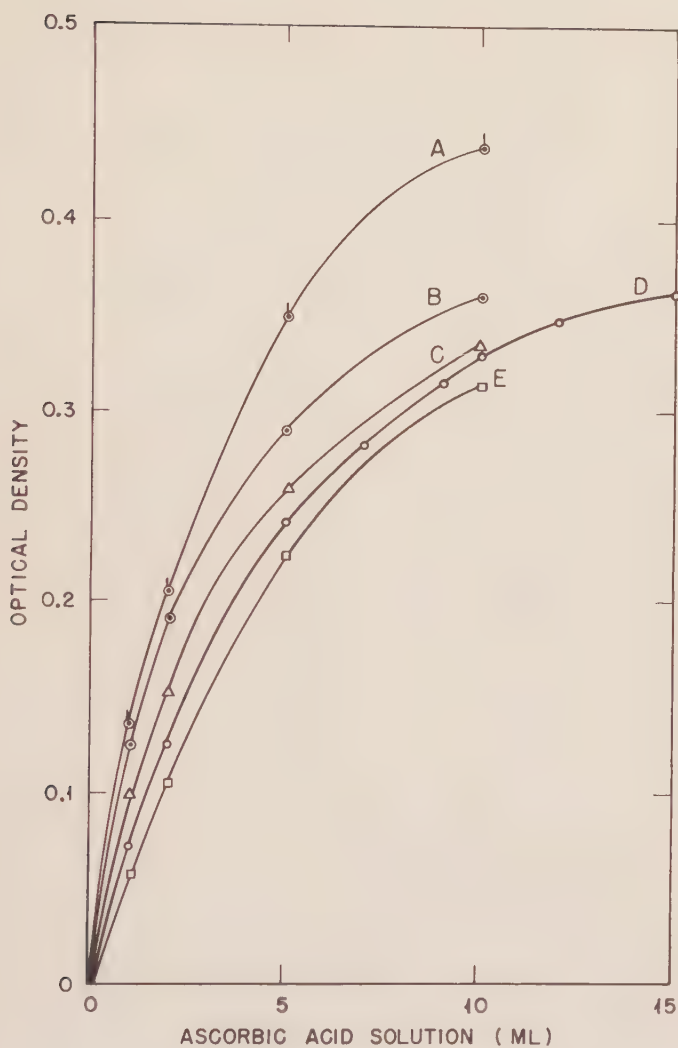


Fig. 1.30—Effect of the buffer-ascorbic acid ratio on the optical density. Solutions were prepared as in Fig. 1.29 by using varying amounts of buffer and ascorbic acid solutions. Curve A, no buffer; curve B, 1 ml of buffer; curve C, 5 ml of buffer; curve D, 8 ml of buffer (according to procedure given); curve E, 10 ml of buffer. The optical densities were measured against water at $400\text{ m}\mu$ with the Beckman spectrophotometer using 1-cm cells.

sample is diluted to 50 ml. The transmittancy of the solution is measured at $410\text{ m}\mu$ against a blank. The uranium concentration is obtained from a transmittancy-concentration curve made from known amounts of uranium under the above conditions.

(2) Determination by Cacotheline. Cacotheline, which has been suggested^{386,387,421} for use in determining micro amounts of uranium,

Table 1.10 — Interferences in the Determination of Uranium
with Ascorbic Acid

Ion	Compound	Ion/uranium, mg	Interference, %
Cl	HCl	2,000	None
NO_3	HNO_3	100–1,000	± 2
SO_4	H_2SO_4	20–80	5–10
PO_4	H_3PO_4	0.02–0.1	5
F	$\text{KF} \cdot 2\text{H}_2\text{O}$	≈ 0.1	5
Oxalate		0.05	2
Tartrate		0.05	2
Citrate		0.05	2
Pb	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	25	*
Mg	MgCl_2	12	None
Al	$\text{Al}(\text{NO}_3)_3$	2–12	≈ 5
Fe		5–10	1–5
Th		1–10	5
Zn		5	5
Cu		≈ 2	5
Mo		1	5
V		0.1	1–5
Cr		0.25	4

*Reported as "no appreciable effect."

has been investigated.^{395,400} The amethyst color produced is due to a reduced form of cacotheline and is formed by several ions. The reduction, although quite reproducible in solutions containing pure uranium, is found to be affected very markedly by the presence of impurities. Copper gives the same color as uranium, and iron(III), nickel(II), chromium(III), and calcium(II) do not give reproducible effects.

Attempts to use the method after ether purification were unsuccessful. The method is therefore not recommended for the determination of uranium.

(3) Determination by Chromotropic Acid. Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has been suggested as a reagent for uranium,^{386,387} but interferences by manganous, ferric,

cupric, and mercuric ions were noted. A method was developed for quantitative determination of uranium using this reagent at pH 10.3 (see reference 391).

The light absorption is such that any convenient wavelength between 400 and 600 $m\mu$ can be used. Beer's law is obeyed over all ranges of concentration, and the color is reproducible. The color produced is stable even after standing for 36 hr.

A number of cations interfere. Sulfate, chloride, nitrate, and perchlorate ions do not interfere, but phosphate, carbonate, and metavanadate ions hinder the color development. The method applies only to substantially pure uranium solutions, which can be obtained in the majority of cases by an ether extraction.

Procedure.³⁹¹ The slightly acidic solution, which contains 0.05 to 2.5 mg of uranium(VI) and is free from interfering elements, is transferred to a 25-ml volumetric flask with carbon dioxide-free water. Five milliliters of chromotropic acid reagent is added; then 5 ml of buffer solution is added. The buffer solution is prepared by diluting 10 ml of hydrochloric acid to 50 ml with carbon dioxide-free water, mixing thoroughly, and removing 12.5 ml. The remainder is cooled in an ice bath and saturated with gaseous ammonia. The 12.5 ml previously removed is added and mixed thoroughly. The solution is used within an hour after preparation. (The chromotropic acid reagent is prepared by dissolving 1 g of chromotropic acid, Eastman Kodak Company, P1613, and 2 g of sodium sulfite in 50 ml of carbon dioxide-free water and filtering; it should be used immediately.)

The solution is diluted to the mark with carbon dioxide-free water and then shaken. The color fades on shaking but returns on standing; it is allowed to develop for 20 min. The transmittancy is read at 460 $m\mu$ against a blank made of the reagents.

(4) Determination by Sodium Cresotate. The use of sodium cresotate was suggested³⁹³ as being more satisfactory than sodium salicylate. No data are given on interferences except for iron and copper; iron and copper must be absent. It is suggested that the reagent be used for solutions of uranyl ions that are free from other cations. The orange color obtained with uranyl ion is stated to be stable and to obey Beer's law. The pH must be carefully controlled and should be about 2.6.

(5) Determination by Sodium Diethyl Dithiocarbamate. Parri⁴⁰⁵ observed that uranyl ion gave a yellow or orange precipitate with ammonium dithiocarbamate in alkaline solution. L. A. Haddock, in unpublished work in 1935, suggested the use of sodium diethyl dithiocarbamate as a reagent for the determination of uranium.^{420a} He found that the uranium complex was not soluble in carbon tetrachloride, but it was soluble in ethyl acetate and ether. Jones⁴²¹ attempted to use

the method for the determination of uranium in urine but found it unsuitable; however, he found the method useful for other purposes. He found that⁴⁰¹ chloroform was a more satisfactory solvent than ethyl acetate-ether, and that the color obtained was stable. The method was investigated further by others.⁴⁰²⁻⁴⁰⁶ The spectral transmittancy

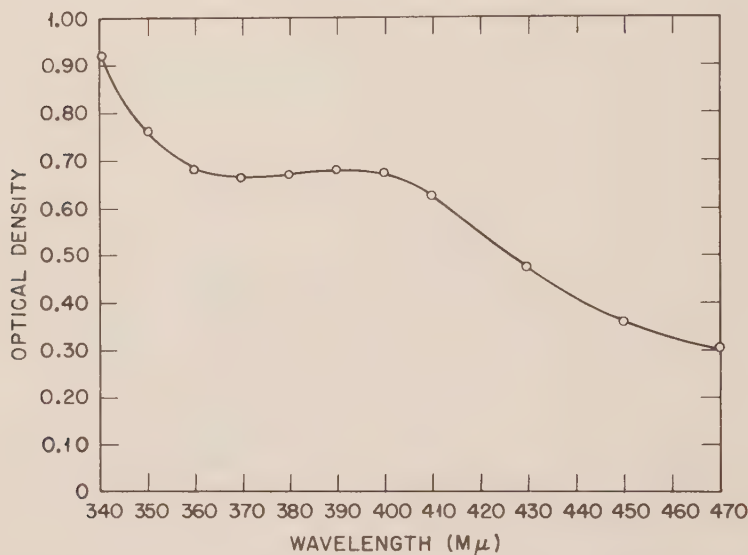


Fig. 1.31 —Spectral transmittancy of uranium diethyl dithiocarbamate solution. Solutions of 2 mg of uranium (slightly acid), 5 ml of 20 per cent ammonium acetate, 6 ml of 2 per cent sodium diethyl dithiocarbamate, and nitric acid to pH 6.8 were made up to 25 ml, extracted with 15-ml portions of chloroform, filtered, and made up to 50 ml, and the optical density was measured against a reagent blank at 380 mμ with a Beckman spectrophotometer using 1-cm cells.

of chloroform solutions was determined by several workers.⁴⁰¹ Figure 1.31 shows the spectral transmittancy of uranium diethyl dithiocarbamate in chloroform from a solution buffered to pH 6.8 before extraction.⁴⁰³ The approximately flat region from 360 to 400 mμ indicates that the wavelength setting is not critical. The reagent itself contributes to the optical density of the solution, and measurements should be made against blanks that contain the same amount of reagent. The color of the uranium diethyl dithiocarbamate has a short period of initial fading, but after 15 min the color is stable for 12 hr. The effect of pH is very marked⁴⁰² from pH 4 to 6 but from pH 6 to 8 the optical density is unaffected by changes in pH.⁴⁰³

The chloroform solutions of uranium diethyl dithiocarbamate follow⁴⁰³ Beer's law up to 6 mg per 100 ml. The sensitivity depends upon the instrument that is used for measurement. An accuracy better than ± 2.5 per cent was indicated.⁴⁰¹ The useful range was from 0.1 to 2 mg of uranium, but this range can be modified considerably.⁴⁰⁶

The large number of interfering elements, such as iron, copper, nickel, cobalt, and others, makes it imperative to use this method only on purified uranium solutions. The fact that the uranium diethyl dithiocarbamate complex is insoluble in carbon tetrachloride, whereas many of the interfering elements are soluble, leads to a separation procedure which was applied for interferences before testing. Reference is made to the procedure used by Jones⁴⁰¹ as given below. It was found that in this purification procedure manganese(II), vanadium, tin, and titanium interfered. This method of purification had its drawbacks because the maximum amount of iron, for example, which could be separated from 2 mg of uranium in 25 ml with a reasonable number of extractions was 10 mg.

Chloride, nitrate, or sulfate did not interfere, but phosphate caused the precipitation of uranium, which was not extractable with chloroform and sodium diethyl dithiocarbamate.

The effect of pH is very pronounced⁴⁰² as shown in Fig. 1.32. The transmittancy is relatively constant between pH 6.4 and 7.4, and the test solution is buffered at pH 6.8.

Preliminary work indicates that the method has some promise, especially after ether extraction.⁴⁰³ It has the drawback of most methods that are based on organic reagents for uranium in that it is not specific.

Procedure.⁴⁰¹ In a 125-ml separatory funnel a solution is prepared that consists of no interfering ions, 2 mg of uranium, 5 ml of 20 per cent ammonium acetate solution, and 20 ml of water. Six milliliters of a 2 per cent solution of sodium diethyl dithiocarbamate is added, and after the pH is adjusted to 6.8, the solution is extracted with four portions of carbon tetrachloride having a total volume of about 30 ml. The aqueous phase is then extracted with three 10-ml portions of CHCl_3 , the extracts are filtered into a 50-ml volumetric flask and diluted to volume, and the optical density is measured at 380 $\text{m}\mu$ against a blank that is carried through the procedure.

It has been found that, if interfering elements are removed by an ether extraction, the optical density of the aqueous solution may be measured. The pH range is 6.5 to 7.2. The sensitivity range is about the same as with the chloroform extraction, and the color is stable for at least 2 hr.⁴⁰³

(6) 8-Hydroxyquinoline Method (Chloroform Extraction). Uranium has been determined by means of 8-hydroxyquinoline. Smales and Wilson⁷¹ used a chloroform solution of the oxyquinolate to determine small amounts of uranium. Greenspan et al.⁴¹¹ have made an extensive investigation of the color developed with 8-hydroxyquinoline in a buffered alcoholic solution. Hubbard⁴⁰⁷ precipitated the uranium with

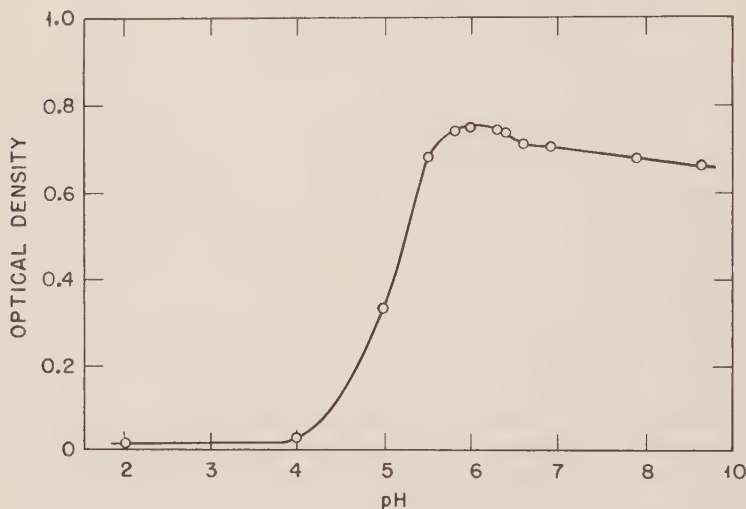


Fig. 1.32 — Effect of pH on the optical density in the diethyl dithiocarbamate determination of uranium.

8-hydroxyquinoline and complexed the uranium oxyquinolate with sulfanilic acid by diazotization. The dye color was developed with sodium hydroxide.

The wavelengths most suitable for the chloroform-extraction method are 425 and 450 $m\mu$.⁴⁰⁹ The color that is produced follows Beer's law up to 2 mg of uranium per 25 ml of chloroform.⁷¹ The interferences are such that a preliminary separation is necessary. Attempts have been made to separate interfering elements such as iron by extracting at pH 2.8 to 4.3 and then by extracting the uranium at pH 7 to 9.3 (see reference 408). An ether-extraction method to purify the uranium has been used with somewhat low recoveries, although it is possibly good enough for control work.⁴⁰⁹ The results, except on pure uranium solutions, are not very promising even after an electrolytic separation of impurities.⁴¹⁰

Procedure.⁷¹ The solution containing no interfering elements is adjusted to pH 7 to 9 with sodium hydroxide and 5 ml of 8-hydrox-

yquinoline solution (1 per cent 8-hydroxyquinoline in 70 per cent ethanol) is added. The uranium complex is then extracted with two successive portions of 5 ml of chloroform. The solution is filtered through a small filter paper, and the transmittancy of the solution is measured at 425 $m\mu$.

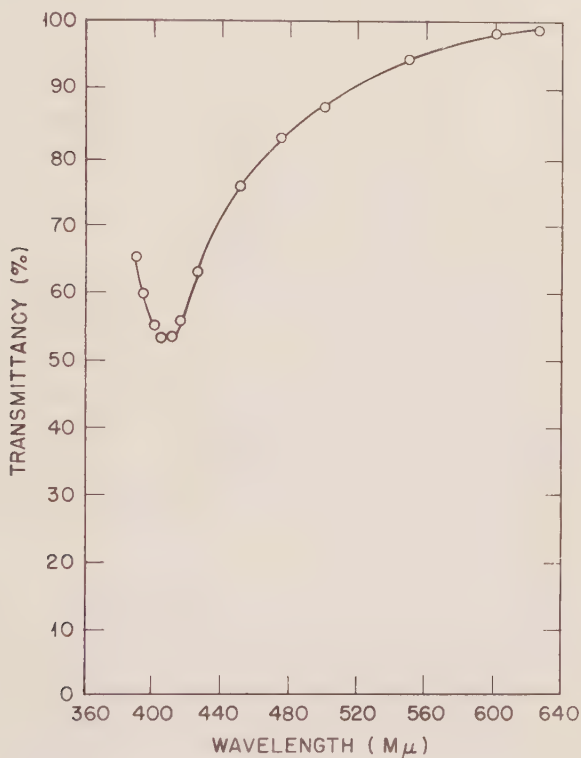


Fig. 1.33—Spectral transmittancy of uranium oxyquinolate in alcohol. A sample of 0.1 mg of uranium as uranium oxyquinolate was measured against 8-hydroxyquinoline blank with a Beckman spectrophotometer using 1-cm cells. The solution contained 2 ml of 35 per cent oxine, 1 ml of uranium solution, and 1 ml of buffer solution (pH 4.4).

(7) 8-Hydroxyquinoline Method (Alcohol Extraction). Work⁴¹¹ on the determination of uranium by using 8-hydroxyquinoline was on materials that have no cations which would interfere. The uranium oxyquinolate is formed in a buffered alcoholic solution, and the transmittancy is read at 500 $m\mu$. The spectral transmittancy of the solution is given in Fig. 1.33. Although the maximum absorption is at about 410 $m\mu$ the alcoholic solution of oxine is very sensitive to pH changes in this region. A wavelength of 500 $m\mu$ is preferred because

in this region the effect of pH is negligible in the range of 4.5 to 7.0. By buffering the solution, reproducible results are obtained, and Beer's law is obeyed.

Since the solutions that were examined contained fluoride ion in nearly all cases, the effect of this ion was studied. Hydrofluoric acid had no effect on the 8-hydroxyquinoline reagent alone, but in concentration greater than 0.05 mg of uranium per milliliter with a fluorine-to-uranium ratio of 3 to 1 there was a definite bleaching effect. Solutions that contained sodium fluoride could not be analyzed. Excess hydrofluoric acid interferes and is removed by evaporation. The transmittancy varies somewhat with the acetate ion concentration, and the buffer solution must be accurately measured. Water, if present in amounts greater than 0.05 ml per 10 ml of solution, causes changes in the transmittancy measurement.

The accuracy of the method has been checked against volumetric determinations with a variation of ± 1 per cent with 1.8 mg of uranyl fluoride per milliliter.

In the range of 0.1 mg of uranium per milliliter the variation is dependent on the instrument and the cells used, but it is usually ± 1 per cent. The solubility of the oxyquinolate complex does not permit higher uranium concentration than approximately 1 mg of uranium per milliliter. By using 10-cm cells it has been possible to determine 0.03 γ of uranium per milliliter in the range of 0 to 25 γ of uranium per milliliter in the cell.

This method was developed for certain conditions of analysis where no common ions are present, and for this purpose it appears sensitive and reproducible. Although the method has been used with uranyl sulfate and uranyl nitrate it is essentially not applicable to other conditions.

Reagents.⁴¹¹ The solutions used and their preparation are given in the following list:

1. Hydroxyquinoline Solution. Exactly 17.5 g of 8-hydroxyquinoline is weighed, dissolved in 95 per cent ethyl alcohol that is at a pH of 7.7, and diluted to 500 ml. The transmittancy of the resultant solution, determined at wavelength of 500 $m\mu$ with a Beckman spectrophotometer using 1-cm cells, should read 85.0 per cent against water as standard. If the transmittancy is lower it is adjusted to 85.0 per cent with ethyl alcohol, or if it is higher it is adjusted with 8-hydroxyquinoline. The resultant solution is stored in a rubber-stoppered pyrex bottle. This solution should last for months with very slight change in its complex-forming properties.

2. Alcohol Buffer Solution (pH 4.40). Exactly 1.5 g of anhydrous sodium acetate is weighed and dissolved in 95 per cent ethyl alcohol,

the solution is diluted to 500 ml, and 88.0 ml of glacial acetic acid is added. The pH as measured by a glass electrode should be 4.40.

3. Alcohol Buffer Solution (pH 4.90). One hundred milliliters of alcohol buffer solution (pH 4.40) is diluted with 100 ml of 95 per cent ethyl alcohol to give a pH of 4.90.

4. Uranyl Fluoride Solution. Uranyl fluoride, 0.1294 g, is dissolved in 0.2 ml of distilled water and diluted to 100 ml with 95 per cent ethyl alcohol. This gives a solution that contains 1 mg of uranium per milliliter. To obtain solutions containing 0.8, 0.5, 0.2, and 0.1 mg of uranium per milliliter, the stock solutions are diluted with appropriate volumes of 95 per cent ethyl alcohol. These solutions are stored in amber-colored rubber-stoppered bottles, placed in a desiccator containing $\frac{1}{2}$ in. of alcohol in the bottom, and kept in the dark. New solutions must be prepared if a precipitate forms. It is important to keep these solutions out of light as much as possible.

Procedure.⁴¹¹ The unknown aqueous solution of uranyl fluoride, which may be prepared from uranium hexafluoride by hydrolysis, is evaporated to dryness in a platinum crucible; an infrared lamp is used for the evaporation to avoid bumping. The sample is then completely dissolved in a minimum amount of water. Not more than 0.02 ml of water per milliliter of final alcoholic uranium solution should be used. The sample is then transferred with 95 per cent ethyl alcohol into a volumetric flask, the volume of which is chosen to give a uranium concentration of 0.02 to 1.00 mg of uranium per milliliter of alcohol.

The colored uranium oxyquinolate solutions are prepared in all cases by adding an alcoholic solution of uranyl fluoride to 8-hydroxyquinoline. One milliliter of an alcoholic solution of known uranyl fluoride content is added to 2 ml of 8-hydroxyquinoline solution and shaken to develop the color. Then 1 ml of alcohol buffer solution (pH 4.4) is added. (The pH of the final solution should be 5.2 to 5.3 by this procedure.) The transmittancy of this uranium oxyquinolate solution is determined at 500 m μ against an 8-hydroxyquinoline standard, which is composed of 2 ml of 8-hydroxyquinoline solution and 2 ml of alcoholic buffer solution (pH 4.90). A transmittancy-concentration curve is constructed using a uranyl fluoride solution of known concentration and following the procedure as outlined.

(8) Diazotized 8-Hydroxyquinoline Method. Another application of 8-hydroxyquinoline to the determination of uranium in the range of 10 to 100 γ has been suggested. In this determination the precipitated uranium oxine complex is centrifuged from the solution and redissolved in HCl-alcohol mixture. The oxine is coupled with sulfanilic acid by diazotization, and the resultant dye is treated with NaOH to give a deep-amber color.

Procedure.⁴⁰⁷ An aliquot of solution containing 10 to 100 γ of uranium and free from interfering substances is pipetted into a 10-ml centrifuge tube, and 1 ml of 8-hydroxyquinoline reagent is added. (The 8-hydroxyquinoline reagent is prepared by neutralizing 5 per cent 8-hydroxyquinoline in 2N oxalic acid with NH_4OH and filtering.) The pH should be adjusted to 5 by adding small amounts of sodium or ammonium acetate or very dilute ammonium hydroxide. The solution is warmed for 10 min in a water bath at 40°C and centrifuged for 10 min. The supernatant solution is decanted, and the mouth of the tube is wiped off before it is reinverted. The precipitate is washed by shaking with 2 ml of water and centrifuged again. Two milliliters of benzene is added to dissolve the excess reagent on the surface, and the liquid is decanted. The precipitate is dissolved with 0.2 ml of dilute HCl (1 to 1), and 0.2 ml of sulfanilic acid reagent (acetic acid plus equal volume of water is saturated with sulfanilic acid) and 0.2 ml of potassium nitrite reagent (0.1 g of potassium nitrite in 2 ml of water) are added. After 10 min the solution is washed into a 25-ml volumetric flask. One-half milliliter of sodium hydroxide solution (20 g of NaOH and 100 ml of H_2O) is added, the solution is diluted to volume, and the transmittancy is measured at 490 $\text{m}\mu$ against a reagent blank. A standard curve is prepared by using the same procedure with known amounts of uranium.

In general, all methods using 8-hydroxyquinoline must have a pure uranium solution and are therefore limited in application.

(9) Determination by Means of Salicylates. Mueller⁴²² suggested the use of an aqueous solution of sodium salicylate for the colorimetric determination of uranium(VI) ion. Ware⁴² has given a review of the use of hydroxy acids of various types as colorimetric reagents for uranium. Kennedy and Segrè⁴¹⁴ used ammonium salicylate for the determination of microgram amounts of uranium. They found that a separation from certain ions, noticeably ferric, was necessary. If triethanolamine is used to complex iron, sodium salicylate can be used to determine uranium in solutions that contain some contaminating ions.⁴¹³ The use of sulfosalicylic acid has been investigated.^{415, 416}

The color developed with salicylate ion depends on the hydrogen-ion concentration. Kennedy and Segrè⁴¹⁴ used ammonium salicylate which developed the color and also acted as a buffer. The color was measured in a visual colorimeter. The wavelength of maximum absorption was not given. An acetate buffer has been used⁴¹² in conjunction with sodium salicylate to obtain pH 7.5. The use of ammonium and sodium salicylate has not been investigated thoroughly, and information regarding the sensitivity and pH effects is incomplete.

Procedure.⁴¹² An aliquot of the sample solution containing 0.5 to 5.0 mg of uranium is transferred to a 15-ml centrifuge tube. The solution is neutralized with 10 per cent ammonium carbonate solution, and 1 ml is added in excess. One milliliter of 3 per cent hydrogenperoxide and 1 ml of 1 per cent aluminum chloride are then added. The pH is adjusted to 8 with ammonium hydroxide, and the solution is diluted to 12 ml. The tube is placed in boiling water for 10 min, cooled, and centrifuged 10 min at full speed. The supernatant solution is decanted into a 50-ml beaker, the sides of the tube are washed down with 5 ml of water, the tube is again centrifuged, and the supernatant solution is decanted into the same beaker. The contents of the beaker are boiled to about half the volume, made slightly acid with nitric acid, and evaporated to 5 ml. After it is cooled, the solution is transferred to a 25-ml volumetric flask, the pH is adjusted to 4 to 5, and the solution is made up to volume. An aliquot containing about 100 γ of uranium is transferred to another 25-ml volumetric flask, and 5 ml of acetate buffer (150 g of ammonium acetate plus 10 ml of ammonium hydroxide per liter) and 5 ml of 10 per cent sodium salicylate are added. The solution is diluted to volume, and the transmittancy is read at 380 $m\mu$ against a blank containing all the reagents carried through the procedure. The concentration of uranium is determined from a standard concentration-transmittancy curve.

The chief disadvantage in the use of salicylate is the interference due to iron. In an attempt to circumvent this interference, Gruen et al.⁴¹³ complexed the iron with triethanolamine and developed the color with sodium salicylate at pH 12.3. The method was devised for use with solutions that contain iron, nickel, chromium, and copper, and because absorption occurs with these elements it was necessary to make optical-density measurements at three different wavelengths—450, 570, and 670 $m\mu$.

The method is not very sensitive for uranium; 2 mg of uranium is necessary for an accurate determination.³⁹⁵ Further, since a preliminary purification is necessary this method has no advantage over other methods that depend upon purification before analysis.

Sulfosalicylic acid has been suggested for the colorimetric determination of uranium.^{415,416} The wavelength for the maximum light absorption by the uranium sulfosalicylic acid is about 340 $m\mu$. The color produced depends on the acidity of the solution, and a pH of 3.6 has been found to be optimum. By adding 1 g of the reagent to a solution of this pH and by measuring the light absorption at 375 $m\mu$, it has been possible to determine 0.35 to 20 mg of uranium in 50 ml of solution. The color that is produced follows Beer's law and is quite

stable. Sulfosalicylic acid is relatively sensitive but suffers the usual disadvantage, namely, many ions interfere.

(10) Determination by Means of Alizarin Red S (Sodium Alizarin Sulfonate). The intense red color, produced upon the addition of alizarin red S to a uranium(IV) solution, has been used for the quantitative determination of traces of uranium.⁴¹⁷ The color intensity is about forty times as great as that produced by alkaline peroxide, but it is unstable, and the transmittancy must be read immediately after addition of the reagents.

At the wavelength of maximum light absorption, 525 $m\mu$, alizarin red S reagent has some absorption, and hence the amount of reagent must be carefully measured. Beer's law is followed if the measurements are made immediately upon addition of the reagents.

The intensity of the color complex is constant in the range of pH 2.2 to 4. It is advantageous to measure the color at the greatest practical acidity in order to minimize the interference that is due to the other ions.

Serious negative errors are caused by fluoride, oxalate, phosphate, copper(II), and iron(II); therefore these ions must be absent. Aluminum, chromium, and cobalt give rise to large positive errors. In general, it is necessary to make an ether extraction prior to the determination.

Procedure.⁴¹⁷ The purified uranium solution is evaporated to dryness in a 100-ml volumetric flask. The flask is cooled, and 2 ml of water, 25 mg of powdered zinc, and 20 drops of 3N HCl are added. The solution is then boiled almost to dryness and cooled; 5 ml of buffer solution (3N in formic acid and 0.6N in sodium formate) and 10 ml of alizarin red S solution (0.05 per cent sodium alizarin sulfonate in water) are pipetted into the flask. The solution is made up to volume, and the transmittancy is measured immediately at 525 $m\mu$ against a blank prepared in the same manner. The uranium concentration is obtained from a transmittancy-concentration curve prepared from known amounts of uranium in the same manner.

3.5 Fluorometric Method. Of all methods available for the determination of uranium in trace quantities, the fluorescence method is by far the most sensitive. The fluorescent properties of uranium when exposed to ultraviolet light were first pointed out by Stokes⁴²³ and by Becquerel.⁴²⁴ Nichols and Slattery⁴²⁵ found that the fluorescence was intensified by fusion with solids such as borax and sodium fluoride. The use of sodium fluoride permitted the visual detection of as little as 10^{-10} g of uranium. Hernegger and Karlik⁴²⁶ were the first to develop this fluorescent property into a quantitative analytical method. The fluorescence of uranium in sulfuric or phosphoric acid

has been used for rough assay purposes.⁴²⁷ The quenching of fluorescence by impurities present in the NaF-U phosphor was described by Papish and Hoag.⁴²⁸

Nichols and Slattery⁴²⁵ tentatively suggested UF_6 as the compound that excited the fluorescence. Evans⁴²⁹ collected UF_6 on NaF- K_2CO_3 beads, but the mixture had to be fused in order to obtain maximum fluorescence. In all probability, judging from chemical evidence the uranium that fused in sodium fluoride is present as UO_2^{++} . Solution of the phosphor in water, followed by evaporation to dryness under an Infraradiator, destroys fluorescence. Re-fusion of the phosphor is necessary to restore the original intensity of fluorescence. Hodgson⁴³⁰ indicated trouble in keeping potassium fluoride fluorescence standard beads because of the effects of moisture. Deliquescence difficulties were overcome by storing his standards in a large sealed pyrex tube. It has been reported⁴³¹ that the carbonate-fluoride phosphor is not affected by moisture.

There are a great many ions that may interfere with the fluorescence method of analysis. Any ion or mixture of ions in the fluorescent disk or bead which causes the apparent content, as obtained by comparison with disks or beads of known uranium content, to be less than the actual uranium content is known as a "quencher," and the degree of quenching is designated as "Q."

The symbol ϕ represents a relative efficiency and may be defined as the ratio of the fluorescence found in any one sample to the fluorescence produced by an equal amount of uranium in the absence of quenching ions. ϕ equals unity when no quenching occurs; when there is 100 per cent quenching, ϕ is 0. The relation between Q, which is the percentage of quenching, and ϕ , which is the coefficient of probability of fluorescence, is

$$Q = 100 (1 - \phi)$$

Quenching is constant in most cases when the concentration of quencher in the flux is constant, even though the uranium concentration varies by a factor of several thousand as illustrated by Fig. 1.34. Figure 1.35 shows the relation between the quenching, as expressed by ϕ , and the amount of quencher. These figures indicate that the critical factor in the quenching phenomenon is the concentration of the quencher in the flux and not the ratio of quencher to uranium.

Since solutions of uranium show fluorescence, but not so strongly as in fused beads or disks, it is highly improbable that quenching is due to changing the state of the uranium ion by an interfering element. Price et al.⁴³² and Kinderman and Newton⁴³³ have derived mathematical explanations of theoretical quenching phenomena.

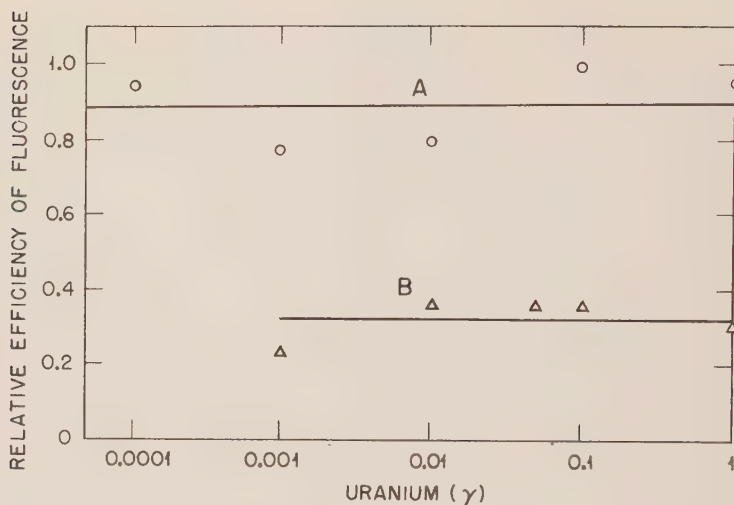


Fig. 1.34—Relation between quenching and the concentration of uranium. Line A, urine with normally occurring quenchers and added uranium; line B, urine with a constant amount of added chromium quencher (10 γ) and added uranium. Two hundred milligrams of NaF was used as flux.

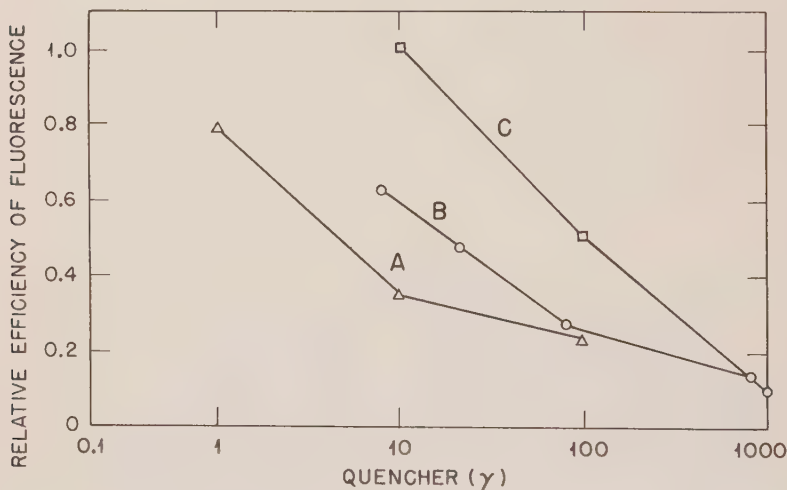


Fig. 1.35—Variation of quenching with concentration of quencher. Curve A, chromium as nitrate + 0.1 γ of uranium; curve B, mixed quencher (equal amounts of Fe, Pb, Ca, Cu, Al, Mg, Bi, Cr, in HNO_3) + 0.1 γ of uranium; curve C, thorium as nitrate + 0.1 γ or uranium. Two hundred milligrams of NaF was used as flux.

(a) Interfering Elements. Elements that are the most commonly encountered contaminants in solutions and solids are iron, chromium, copper, calcium, and silicon. Elements and ions which present more specific interferences but which are not so common and normally are not present in such high concentration as the previous five are molybdenum, cerium, columbium, vanadium, zinc, nickel, tin, aluminum, rubidium, magnesium, titanium, sulfate, chloride, and phosphate. Specific ion interferences, methods of elimination, and allowable concentrations are discussed under each method considered applicable to trace determinations of uranium.

Investigations have been made in regard to the quantity of ions other than uranium which act as quenchers. A summary of tolerances and effects of addition of foreign ions above allowable limits⁴³⁴⁻⁴³⁷ is presented in Table 1.11.

Some of the substances tested, particularly molybdenum, strontium, magnesium, nickel, and lead, showed variable quenching;⁴³⁴ the results given are for the maximum quenching found.

In order to determine whether sufficient interfering elements are present to result in quenching of the emitted fluorescent light, the "spiking" or "addition" technique may be employed. The basis of the spiking technique is that the same proportion of added uranium would be quenched as the uranium that is present in the original sample. This procedure can be applied to any individual fused disk or bead by making the initial reading and repeating the fusion and reading after a known amount of uranium is added. If the difference between the second and first reading is equal to the amount of uranium added, no quenching has occurred.

If quenching occurs the safe procedure is to remove all substances not known to be harmless by a method that has been examined and proved to be satisfactory for the type of sample concerned.

Another method of overcoming the quenching of emitted fluorescent light by interfering ions is the "dilution" technique. The dilution technique is employed on the basis that ϕ approaches 1 as the concentration of quencher is decreased. It is possible to reduce quenching to a negligible factor by using a sufficiently small aliquot for analysis and by using the same amount of flux. Phosphors, made from solutions containing quenching ions and uranium, show less quenching as the solutions are progressively diluted as indicated in Fig. 1.36. Application of the dilution technique is limited to solutions in which quenchers are not present in ratios exceeding 1,000 to 1 (quencher to uranium) and for which an instrument of sufficient sensitivity is employed.

In addition to interfering ions that cause quenching of emitted fluorescent light, a high ratio of uranium to sodium fluoride can quench

Table 1.11 — Empirical Quenching Data Obtained by Fusing 2.5 g of Flux (2.5 Per Cent KF and 97.5 Per Cent NaKCO₃) with 1.0 γ of Uranium Followed by Addition of the Quencher in Solution and by Re-fusion of the Disk

Quenching ion	Amount of ion, mg			
	$\phi = 1.0$	$\phi = 0.9$	$\phi = 0.75$	$\phi = 0.5$
Ag		0.001		0.5
Al	50*			
Au		0.005	0.02	0.15
B as H ₃ BO ₃	1	1.5	2.5	3.5
Ba	0.5	5.0	>50	
Be	1			
Br	1,000*			
Ca	0.1	1.0		15.0
Ce		0.02		0.2
Cl	250*			
ClO ₄		0.5		1.5
Co		0.001		0.01
Cr(III) or (VI)		0.001		0.01
Cu		0.01		0.05
Fe(II) or (III)		0.003		0.06
Hg†	≈ 0.005			
Li‡	1	2	3.5	6
Mg§		0.05		0.65
Mn(II) or (VII)		0.002		0.01
Mo as molybdate§	0.5	1.0	>100	
NH ₄	Volatilized			
NO ₃		0.3		1.8
Ni§		0.001		0.1
PO ₄	1	>50		
Pb§		0.002		0.1
Pt		0.005		0.1
SiO ₂ as Na ₂ SiO ₃	0.1	1		13
Sm		0.15		0.8
SO ₄	350*			
Sn(II)		0.05	0.5	2
Sr§	0.1	1	>50	
Sn(IV)		0.05	10	
Th		0.015		0.15
Ti in H ₂ SO ₄ ¶		0.05		0.5
W	0.02	0.5	100	
Zn		0.028		0.15
Zr	1			
V as vanadate	30*			

* Maximum tested.

† All but a trace is vaporized during fusion.

‡ Quenching complete ($\phi = 0$) at approximately 7.5 mg unless more fluoride is added.

§ Variable quenching.

¶ Greenish fluorescence when more than 0.2 mg of Ti is present.

fluorescent light^{425, 438} as shown in Fig. 1.37. The intensity of fluorescent light varies in a linear manner with the uranium content until the bead content contains about 10^{-5} mole U per mole NaF.⁴²⁶ Essentially the same relation has been found when the NaF-Na₂CO₃-K₂CO₃ flux was used.⁴³⁹

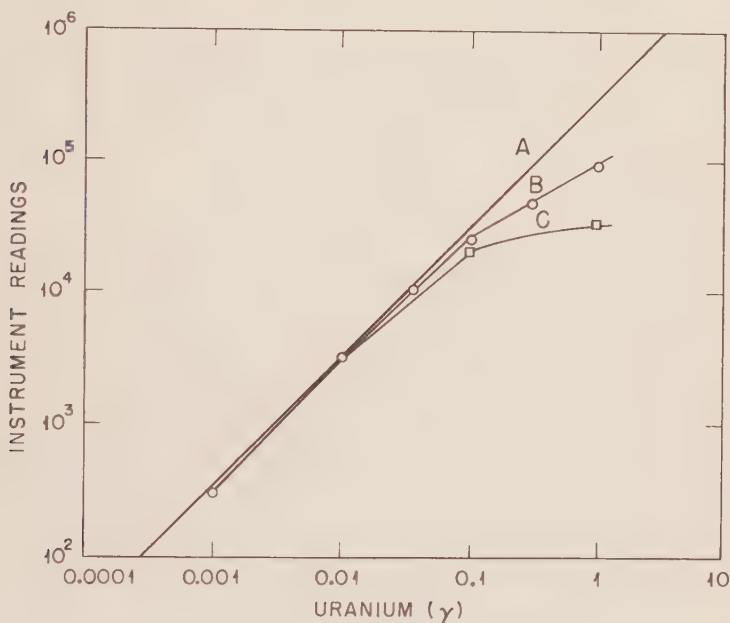


Fig. 1.36 — Variation of fluorescence with dilution. Curve A: Uranium with no quencher. Curve B: Uranium plus mixed quencher. (Mixed quencher has the same composition as in Fig. 1.35.) Uranium was added to mixed quencher to have a final ratio of 72 of quencher to 1 of uranium. This solution was progressively diluted and a portion was added to the sodium fluoride flux. Curve C: Uranium plus iron. Uranium was added to a ferric nitrate solution to yield an iron-to-uranium ratio of 1,000 to 1. Progressively diluted samples of the solution were used as in curve B. Two hundred milligrams of NaF was used as flux.

A few elements that interfere with the fluorescence analysis do not quench but enhance emitted fluorescent light. Columbium⁴²⁸ and tantalum show some fluorescent properties if fused with sodium fluoride. Five hundred micrograms of columbium gave the same fluorescence as 0.3 γ of uranium, and 50 γ of tantalum gave the same fluorescence as 0.6 γ of uranium.⁴³⁷ This fluorescence may have been caused by a trace of uranium in the columbium or tantalum. Neodymium, columbium, and tantalum were examined by Price et al.,⁴³² who concluded that no known element interfered with the determination according to their procedure.

Salts of beryllium are known to fluoresce,⁴⁴⁰ but when 1 mg of beryllium was treated in a manner similar to uranium no measurable fluorescence was found.

The minimum quantity of uranium detectable by the fluorescence method of analysis is 10^{-11} g of uranium in a phosphor made with a

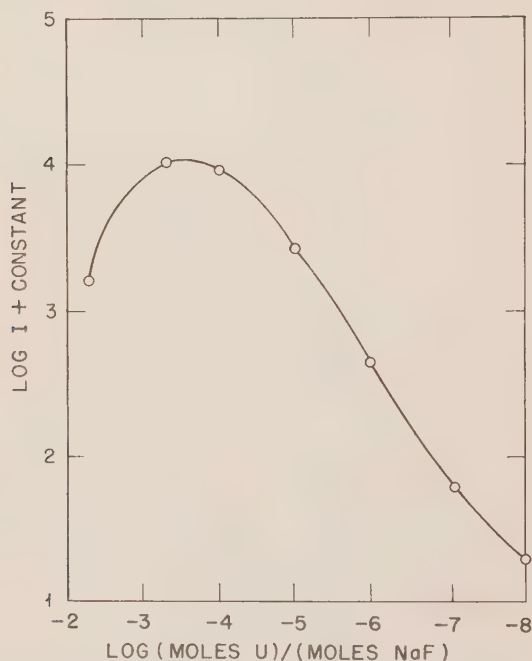


Fig. 1.37—Variation of fluorescence intensity vs. the ratio of uranium to sodium fluoride. Phototube, IP21, was used to measure the light intensities. Corrections were made for the light because of the blank (see reference 438). Twenty milligrams of NaF bead was used as flux.

flux of 200 mg of pure sodium fluoride.⁴³² The accuracy in such concentrations is extremely poor owing partially to fluorescence caused by impurities in the flux.

Visual comparison with standards has been used successfully for uranium contents up to 50γ . Through most of this range, disks that differ by less than 5 per cent in their uranium content can be readily distinguished. The lowest level found useful is 0.01γ , though smaller amounts can be detected. The range recommended for visual comparison is from 0.1 to 2.0γ ; use of a wider range requires an inconveniently large number of standards. Photometric measurements

have shown that the intensity of fluorescence varies linearly with the uranium content up to at least 50 γ . If a fluorometer is used, the best range will depend on the instrument employed.

Neuman,⁴⁴¹ when using a flux of 75 mg of sodium fluoride, found the range and accuracy shown in Table 1.12 applicable.

An accuracy of ± 5 per cent utilizing the fluorescent-bead test to chemically purified solutions of uranyl nitrate has been reported.⁴⁴² A precision of approximately ± 5 per cent has been obtained by employing ether extraction of uranyl nitrate solutions as a means of

Table 1.12 — Range and Accuracy of Fluorescence Analysis According to Neuman⁴⁴¹

Type of material	Analysis range	Accuracy
Pure uranium solutions	0.001–0.3 γ	Standard error, 0.003 γ
Urine	Minimum, 0.01 mg/liter	Average deviation, 11 per cent
Tissues	Minimum, 1 γ /g	Recovery, 85 per cent
		Standard deviation, 8 per cent

purification and by reading the phosphor in a fluorometer.^{443,444} The working range was reported to be in concentrations of less than 10 mg of uranium per liter.

Kinderman and Newton⁴³³ report a precision within 4 per cent after removal of quenching ions from the uranium solution. A Duboscq-type colorimeter was used to read the beads.

The most common source of error in the fluorescence method of analysis is the presence of ions that cause quenching. The amount of this error can be determined by the spiking method as outlined previously. Dust that contains uranium is a source of error. Handling a bead with contaminated hands or allowing it to contact a contaminated surface prior to sample addition and final fusion leads to high values. Inadequate cleaning of the phosphor container, platinum dish, gold dish, silver dish, or platinum loop may give high results owing to residual contamination.

Each time a fresh batch of reagent is used a blank should be run to assure absence of any fluorescence resulting from contamination of the reagent. Sodium fluoride in some instances was found to impart fluorescence above the allowable limits because of impurities.⁴³²

Variations in fusion and cooling techniques can account for non-reproducibility of some determinations on phosphors. Fusion over a reducing flame decreases to 20 per cent of its normal intensity the fluorescence caused by 1 γ of uranium. If cooling in the air is taken as the standard procedure, more rapid cooling with ice causes a slight reduction in the fluorescence of the phosphor. Cooling slowly in the

oxidizing flame of a Meker burner results in an increase of about 30 per cent in the fluorescence. Fusions in platinum in a muffle furnace or a closed system at 1000°C resulted in quenching due to solution of platinum.⁴³⁵ The most important factor in all fusion operations is the standardization of conditions. That is, samples should be fused for the same length of time and under the same conditions as the standards.

If visual comparison is used as the method of determining the intensity of fluorescence, errors result unless at least 2 min is allowed, to accustom the reader's eyes to darkness after entering the dark room, before comparison of the phosphors under the ultraviolet radiation. Unless goggles with filters to transmit 520 to 640 m μ radiation are worn, variability in results may be encountered.

(b) Flux Material. The flux used in fluorescence methods has varied considerably.

Pure NaF (see references 432, 442, 445, and 446) has been used extensively in fluorescent-bead tests with a maximum sensitivity to less than 10^{-11} g of uranium. The primary difficulty in employing sodium fluoride, however, as a flux is that the melting point is high (992°C).

Other fluxes, possibly not quite so sensitive as sodium fluoride, which have been employed with visual comparison, fluorophotometer, and the Duboscq-type colorimeter are: 48.3 per cent K_2CO_3 , 49.9 per cent Na_2CO_3 , and 1.8 per cent NaF;⁴⁴⁷ 55 per cent Na_2CO_3 , 42.5 per cent K_2CO_3 , and 2.5 per cent KF;⁴³⁷ and 9 per cent NaF, 91 per cent $NaKCO_3$.⁴⁴⁸ The last-mentioned flux gives a sensitivity very near that of fused sodium fluoride, as is shown in Fig. 1.38, and is neither as difficult to fuse nor as deliquescent as pure sodium fluoride.⁴⁴⁹

It is imperative that all reagents be checked to ascertain complete absence of fluorescence because of impurities. The flux should be thoroughly mixed in a scrupulously clean, dry ball mill, using clean dry granite balls, and should be stored in airtight containers.

If platinum dishes are used, the fusion of the phosphor must be carried out at the lowest temperature possible, and yet a thorough and complete fusion must be obtained. No significant amount⁴³⁴ of platinum has been found in melts prepared in which fusion ($NaKCO_3$ -NaF phosphors) is accomplished below 750°C. Higher temperatures should be avoided, because large amounts of platinum (nearly a milligram) have been dissolved from the dish at approximately 900°C, resulting in almost complete quenching, as shown in Table 1.11.

(c) Fluorescence Standards. Preparation of permanent-type standards for fluorescence analysis has been attempted. Permanent glass fluorescence standards were prepared from various mixtures of pyrex, Canary glass, and an orange fluorescence glass. Fluorescence

of these standards was off-color and did not exactly match standard disks made of fusion mixture and known amounts of uranium. Duco Household Cement thinned with acetone was a satisfactory coating for fluorescent beads for a month.⁴⁵⁰ Some batches of this cement exhibited a slight bluish fluorescence and had a tendency to turn yellow when exposed to ultraviolet radiation. A disk of methyl methacrylate

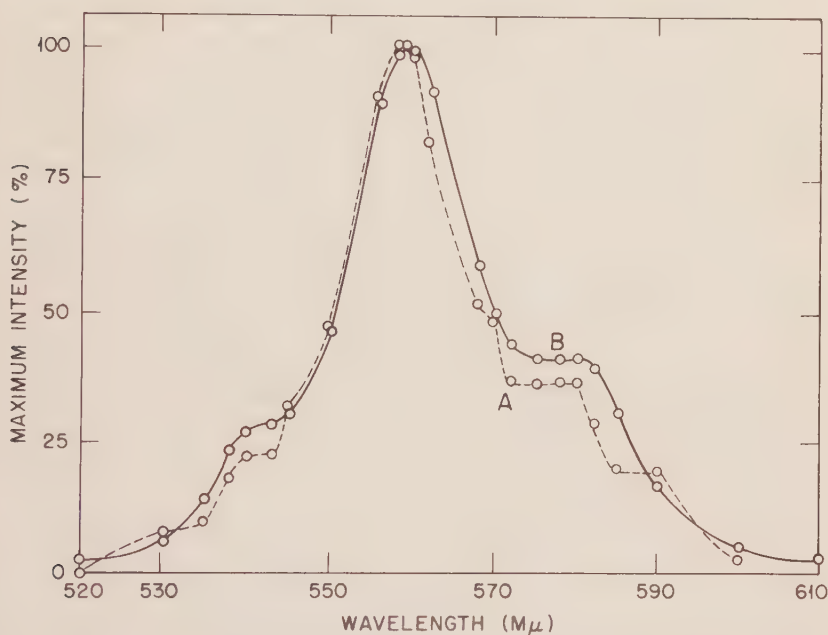


Fig. 1.38—Variation of fluorescence with flux. Curve A, 0.125 mg of uranium per 2.5 g of flux consisting of 9 per cent NaF and 91 per cent NaKCO₃; curve B, 1.6 mg of uranium per 2.5 g of NaF. Measurements were made with Beckman spectrophotometer which is adapted for fluorescence measurement; the slit width was 0.2 mm.

emitted fluorescent light and developed a yellow color after it was exposed to unfiltered ultraviolet radiation for 24 hr.⁴³¹ A study of the effect of coating fluorescence standard disks with very thin coats of methyl methacrylate indicated that coating enhanced fluorescence standards by an amount equivalent to about 0.05 γ of uranium per disk. The extreme heat from the ultraviolet radiation caused the thin layers of methyl methacrylate to blister and crack.⁴⁵¹ In general, permanent standards have not proved practical.

(d) Apparatus for Visual Observations. A great many different types of ultraviolet lamps have been used.

1. CH-4 Lamp, 100 watt, Westinghouse Electric & Manufacturing Co.
2. Conti-Gloe, model 96, 100 watt, Switzer Bros., Cleveland, Ohio.
3. EH-4 Lamp, 100 watt, and AH-2 Lamp, 250 watt, General Electric Company.
4. Zyglo Fluorescent Lamp with CH-4 Lamp, 100 watt, Magnaflux Corporation, Chicago.
5. Inspectorite with EH-4 Lamp, 100 watt, and Utility Model with No. S353 Lamp, 100 watt, Hanovia Chemical & Mfg. Co.

In many of the above, it is desirable to use a constant-voltage transformer in conjunction with the transformer supplied. Satisfactory filters for the light source include Corning No. 5860, 5874, or 5875 of at least 5 mm thickness. Any of these will satisfactorily filter out visible light without seriously reducing the ultraviolet output. Filters used in reading the intensity⁴³⁸ of emitted fluorescent light are 5 mm in thickness, Corning No. 3484 or 3389 (Noviol "A") alone, or in conjunction with Corning No. 9780.⁴⁴⁵ Goggles that will transmit light in the range of 520 to 640 m μ should be worn when visual comparison is made, because ultraviolet radiation is extremely harmful to the eyes. If visual comparison is used as a means of determining the intensity of fluorescence, a dark room is necessary.

For a discussion of photofluorometers that have been employed see Chap. 24 on "Photometric Methods."

(e) Containers. Various phosphor containers have been utilized. A 2.5-cm section of 0.5- to 0.8-mm platinum wire fused into the end of a short piece of pyrex tubing with a uniform loop 3 mm in diameter serves very well as a holder or container in the bead test for fluorescence analysis.⁴³⁸ Dishes of platinum, silver, and gold have been successfully utilized in many laboratories. It is necessary to use a platinum dish if sodium fluoride is to be used as a flux because of its relatively high melting point. Gold dishes, which are stamped from gold sheets 3.5 by 3.5 by 0.0635 cm, with a working depression of 3 mm depth and 3 cm diameter have proved satisfactory. Platinum crucible covers, 25-ml standard form, were also used for routine use since they are available commercially. It was found advisable to re-die new lids to a depth of 3 mm. Platinum cups that have circular indentations 11 mm in diameter and 1.6 mm in depth were used by Neuman.⁴⁴⁵

The above discussion is based on reports from different laboratories, and some are at variance. In general it may be stated that the fluorescence method is very satisfactory when used under standard conditions.

While the statements as to the necessity of removing quenching elements may be confusing, this is chiefly because of the instruments used for observation. If an instrument is employed that has the necessary sensitivity, then the dilution technique may be employed and the necessity for removal of quenching elements can usually be eliminated. These instruments are generally very costly and require more care than some of the less sensitive instruments. With the less sensitive fluorometer it is usually advisable to remove the quenching elements. This is not too serious a handicap because in most cases it is necessary to dissolve the material in order to obtain a representative sample. If this is not done when the dilution technique is employed, erroneous results may be obtained. After the sample is dissolved, an ether extraction of the nitrate readily separates the uranium from interfering elements.

(f) Fluorescence Procedures. There are two primary methods for the determination of uranium which utilize its fluorescence properties as a basis of analysis. Although the principle and theory regarding each method is identical, they differ in detail to such an extent that both will be discussed separately.

(1) Fluorescent-bead Method.⁴³⁸ The fluorescent-bead test may be applied to a chemically purified sample of uranium nitrate. The general order of magnitude may be determined in the presence of small amounts of iron, copper, sulfate, chromium, nickel, and manganese.

Procedure.⁴³⁸ Pills of pure sodium fluoride are made by pressing powdered sodium fluoride into holes 0.113 in. in diameter; these holes are bored through 0.125-in. bakelite sheets placed on clean plate glass. The pill of sodium fluoride is pushed into the depression of a clean spot plate. A platinum-wire loop of 3-mm diameter is heated to redness in a Meker flame, the pill is scooped up on the hot wire, and the sodium fluoride is fused so that the loop is completely filled. Each bead thus made is checked against a blank bead under ultraviolet radiation to assure absence of background fluorescence. The bead is carefully protected from any surfaces that may be contaminated with uranium or interfering ions and is stored under a glass bell jar until ready for use.

To deliver the solution to the bead, an oval platinum-wire loop is formed (about 3 by 6 mm), which will just fit over the beads. The delivery loop is dipped into the solution to be used and then slipped over the bead to transfer the solution. To determine what amount of solution is delivered, the platinum loop may be calibrated by weighing it before and after a drop is delivered.

The bead is dried under a radiant heater and fused in a Meker flame until clear. After it is cooled the bead is compared, either visually

or under a colorimeter, against a set of standard beads. These beads were made, as mentioned above, from solutions that contain 0, 0.125, 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, 16.0, and 32.0 γ of uranium on a 20-mg bead. A Duboscq colorimeter may be employed to increase the accuracy of the reading. The colorimeter cups are filled with 5 per cent copper sulfate solution, and a Noviol No. 3389 filter, 5 mm thick, is mounted on the eyepiece. (A solution containing 10 to 15 mg of "monocarbazyl dye" in 0.1N HCl may be used instead of the copper sulfate solution.)⁴⁴⁴ The beads are held under the colorimeter by means of a bakelite jig, which is held in position by a clamp. The ultraviolet source is mounted over the beads at a 45-deg angle to the line of sight. For an illustration of the instrument used reference is made to Chap. 24 "Photometric Methods."

(2) Fluorescent-disk Method. The fluorescent-disk method is applicable to solutions that contain 0.05 to 30 γ of uranium per milliliter. The different procedures and instruments used vary only in detail.

Procedure.⁴⁴⁸ The solution of uranium from which the impurities have been removed by an ether extraction is transferred to a dish and evaporated to dryness. If the sample contains an appreciable amount of organic matter, it is ashed by heating briefly in a bunsen flame. The flux (2.5 g: 9 per cent NaF, 91 per cent KNaCO_3) is added and fused over a Meker burner. Platinum dishes are held with ordinary platinum-tipped tongs, and the flux is not allowed to run out of the depression. Gold dishes are held with special tongs that do not touch the upper surface, and the molten flux is made to run over all the upper surface to pick up any material that may have "creeped," and then the flux is drained back into the depression. This is easily done with the gold but not with the platinum, which is wet by the flux. When cold the flux forms a disk $1\frac{3}{8}$ in. in diameter and about $1\frac{1}{2}$ mm in thickness at the center. The flat dishes with their disks are measured in the fluorometer. (See Chap. 24 on "Photometric Methods.")

Procedure.⁴³² No preliminary purification is employed. The material to be analyzed is dissolved in, or diluted with, nitric acid. One-tenth milliliter of this solution is pipetted into a platinum dish approximately $\frac{1}{2}$ in. in diameter and evaporated to dryness under an infrared lamp. If the sample contains an appreciable amount of organic matter, it is ashed by heating briefly in a bunsen flame. Concentrated nitric acid may be added, and the evaporation may be repeated if necessary. Two hundred milligrams of sodium fluoride is then added to the dish. It is held with a pair of platinum-tipped forceps over a Meker flame to fuse the sodium fluoride, which is kept in the molten state for about 15 sec. After it is cooled, the dish is

placed in the holder of a photoelectric instrument. (See Chap. 24 on "Photometric Methods.") The galvanometer deflection is read, an Ayrton shunt being adjusted so that the scale reading lies between 10 and 100. The scale reading is multiplied by the shunt ratio, the value of the blank is subtracted from the reading obtained, and the amount of uranium contained in the dish is found by multiplying the difference by a previously determined factor.

4. SELECTED PROCEDURES

4.1 Introduction. The selected procedures which follow are those that illustrate the main features of the previous sections of this chapter. These procedures are used in the field of ore and mineral analysis. In the analysis of these materials, the solution of the sample, which may consist of complex minerals, the separation from various interfering elements, and the determination of the uranium are well illustrated.

4.2 Gravimetric Determination in Ores. Sulfide-Carbonate-Hydroxide Method. The sample is decomposed with nitric and sulfuric acid. Arsenic is removed with hydrobromic acid; the acid sulfide metals are removed with hydrogen sulfide; aluminum, chromium, and iron are removed with ammonium hydroxide-ammonium carbonate; and cobalt and nickel are removed with hydrogen sulfide in ammoniacal solution. The solution is then acidified with hydrochloric acid, and the uranium is precipitated with ammonium hydroxide. The ammonium hydroxide precipitate is calcined in a muffle furnace at a bright-orange heat and weighed as U_3O_8 .

Procedure.⁴⁵² A sample weighing 3 to 5 g is digested for 20 to 30 min in 15 ml of H_2SO_4 and 15 ml of HNO_3 . The solution is heated over a bunsen burner until dense white fumes are given off; care must be taken to keep the contents swirling. The residue is cooled, 10 ml of HCl and 10 ml of HBr (1 to 1) are added, and the heating is repeated with a swirling motion, as above, until dense white fumes of SO_3 are given off.

The solution is cooled and diluted to about 300 ml. It is then boiled to dissolve all soluble material and is stirred constantly to avoid bumping. The solution is cooled to slightly below room temperature, H_2S is passed into it for 20 to 30 min, and it is then filtered through a Whatman No. 30 filter paper whereupon silicon, lead, silver, copper, cadmium, and antimony are removed in the insoluble precipitate. The residue is washed well with H_2S water. The filtrate is boiled to expel the H_2S , and saturated bromine water is added slowly until a deep bromine color persists (to oxidize any remaining sulfides). The

boiling is then continued to remove the excess bromine. Ammonium hydroxide (1 to 3) is added slowly to the hot solution until a precipitate begins to form; 2 to 3 ml of saturated $(\text{NH}_4)_2\text{CO}_3$ solution, NH_4OH (1 to 3) in slight excess, and two or three cubes of $(\text{NH}_4)_2\text{CO}_3$ are added; then the solution is stirred for 1 to 2 min. The precipitate is allowed to settle, is filtered on a Whatman No. 30 filter paper, and is then dissolved in HCl (1 to 3). The solution is boiled, the above precipitation with NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ is repeated, and the filtrate is combined with the former. (In case of very low-grade samples, which contain large amounts of ammonium hydroxide-group elements, a third separation may be necessary.) The precipitate is washed well with a solution of $(\text{NH}_4)_2\text{CO}_3$. The volume of the filtrate is now about 450 to 500 ml.

Hydrogen sulfide is passed into the filtrate to precipitate cobalt and nickel. The solution is allowed to stand for several hours to permit the fine precipitate to conglomerate. It is then filtered on a Whatman No. 42 filter paper, the funnel being kept well filled at all times. The precipitate is not washed. The filtrate is acidified with a slight excess of HCl (1 to 3) and boiled to expel CO_2 and H_2S , and saturated bromine water is added to oxidize any remaining sulfide.

The solution is removed from the hot plate, and NH_4OH (1 to 3) is immediately added drop by drop to precipitate the uranium. The end point is apparent when the liquid changes color from pale yellow to colorless except for the turbidity caused by the precipitate. A slight excess of NH_4OH is advisable. The solution is boiled 1 min to coagulate the precipitate and is filtered while hot through a Whatman No. 42 filter paper; it is then washed well with hot recently boiled distilled water.

The precipitate is placed in a tared porcelain crucible, dried well, and heated slowly in a muffle furnace in order to burn the paper without flaming. It is then heated at a bright-orange heat for at least 30 min in an oxidizing atmosphere, cooled in a desiccator for 2 hr, and weighed as U_3O_8 .

4.3 Volumetric Determination in Ores. (a) Sulfide-Carbonate-Phosphate-Permanganate Method. In this method the sample is decomposed with nitric acid and sulfuric acid, and the acid sulfide metals are removed with hydrogen sulfide. Metals such as iron are removed by a sodium carbonate precipitation, and uranium is separated from vanadium by precipitation as the phosphate. The phosphate precipitate is dissolved in sulfuric acid, and the uranium is reduced in a Jones reductor and titrated with potassium permanganate.

Procedure.⁹⁶ Two 1-g portions of the finely ground material are weighed into glass-stoppered weighing bottles. The bottles and con-

tents are dried for 2 hr at 110°C , and the stoppers are placed on the bottles, which are cooled to room temperature and weighed. The contents are poured immediately into 400-ml beakers, and the empty bottles are weighed.

The material is decomposed by warming with 10 ml of HNO_3 (1 to 1) and 10 ml of H_2SO_4 , the heating being continued to strong fumes of SO_3 . After it is cooled, the sample is diluted with water to a volume of about 150 ml, boiled, and allowed to cool for at least 2 hr. The lead sulfate, etc., are filtered off, and the filtrate is received in a 400-ml beaker. The precipitate, after being washed with cold water, is discarded.

The solution is heated to boiling, and H_2S gas is passed in for about 15 min. The solution is again brought to the boiling point, and hydrogen sulfide is passed in for another 10 min.

The solution is filtered into a 600-ml beaker, and the sulfide precipitate is washed with H_2SO_4 (1 to 99) saturated with H_2S . The precipitate is discarded. The excess hydrogen sulfide in the filtrate is removed by boiling, but if the solution becomes turbid when boiled, the saturation with H_2S is repeated, and the solution is then filtered.

When all the H_2S has been removed the solution is cooled and oxidized by adding 10 to 15 ml of 3 per cent H_2O_2 . To a volume of 150 to 175 ml enough sodium carbonate (solid) is added to render the solution definitely alkaline and then about 3 g in excess. The solution is boiled for 15 min and filtered into an 800-ml beaker. The precipitate is washed with hot sodium carbonate solution; then it is washed back into the original beaker and dissolved with 10 ml of H_2SO_4 (1 to 1). The sodium carbonate precipitation is repeated as before, the solution is filtered through the original filter paper into the original beaker, and the precipitate is discarded.

Five grams of ammonium phosphate is added to the combined filtrates. The solution is then carefully made acid with 30 ml of H_2SO_4 (1 to 1) and boiled to expel carbon dioxide. The uranium is precipitated as phosphate by adding to the boiling solution (400 to 450 ml volume) a slight excess of NH_4OH (1 to 1) followed by a slight excess of acetic acid. The solution is cooled in ice water for about 30 to 45 min and is filtered through $12\frac{1}{2}$ -cm filters, using paper pulp. The precipitate is washed with a water solution that contains 2 per cent ammonium sulfate made slightly acid with acetic acid. When only a small amount of vanadium is present, one phosphate separation is sufficient; otherwise a second precipitation is necessary.

The precipitate is transferred to the original beaker and dissolved in 5 ml of H_2SO_4 and 15 ml of H_2O . The hot solution is passed through the paper in order to dissolve the remaining traces of the precipitate,

and the paper is washed with H_2SO_4 (1 to 95) into a 400-ml beaker. The solution is evaporated cautiously to light fumes of sulfur trioxide and is oxidized by the addition of some finely ground crystals of potassium permanganate.

The oxidized solution is diluted to 150 ml with cold water. The solution is warmed if crystals are present, then it is cooled to room temperature and passed through a Jones reductor; the flow of the solution is regulated so that it takes about 5 min for the total volume to pass. The reductor is washed thoroughly with cold H_2SO_4 (3 to 97). Air is bubbled through the solution for 10 min, and the solution is titrated with standard potassium permanganate.

(b) Sulfide-Cupferron-Dichromate Method. The sample is decomposed with nitric acid and sulfuric acid and is converted to sulfate by fuming. Heavy metals are removed with hydrogen sulfide, and iron, titanium, and others are removed by a chloroform extraction of the cupferrates. The cupferron in the solution is destroyed, and the uranium is reduced in a Jones reductor and aerated and titrated with potassium dichromate.

Procedure.⁴⁵³ A 2-g sample of the ore is weighed into a 250-ml beaker, moistened with water, and covered with 30 ml of HNO_3 (1 to 1) and 12 ml of H_2SO_4 (1 to 1). The beaker is then covered with a watch glass and placed on a hot plate at low heat for 2 hr. The watch glass is tipped, the heating is continued for 1 hr, and then the heat is increased until fumes of SO_3 are evolved. After fuming 3 to 5 min, the sample is allowed to cool, 90 ml of water is added, and the beaker is heated almost to boiling to bring all soluble material into solution.

The solution is transferred quantitatively without filtering into a 500-ml suction flask, water being used as a rinse liquid. The neck of the flask is loosely stoppered, and H_2S under slight pressure is passed in through the side arm for a 30-min period; after this the flask is sealed by closing the neck and side arm with stoppers, and it is then allowed to stand overnight. The solution is then filtered through a Whatman No. 40 filter paper; the paper and precipitate are washed thoroughly with dilute H_2SO_4 (1 to 19) that is saturated with H_2S . The combined filtrate and wash solution, which should have a volume of about 225 ml, is evaporated to 90 ml on the steam bath. If sulfides precipitate, the hydrogen sulfide treatment and subsequent filtration, washing, and evaporation must be repeated.

Ten milliliters of H_2SO_4 (1 to 1) is added to the evaporated filtrate, and the solution is heated to boiling. Potassium permanganate, 2 per cent, is added until the solution is permanently pink; it is then cooled to below 5°C in an ice bath. The solution is transferred to a 300-ml separatory funnel, 25 ml of 6 per cent cupferron solution is added,

and the separatory funnel is shaken for 1 min. Twenty-five milliliters of chloroform is added, and the funnel is again shaken for 1 min. After the solution separates, the chloroform layer is drawn off, but a little chloroform is left in the funnel to prevent loss of uranium with the aqueous layer. The extraction is repeated as above until the chloroform layer is pale green or colorless. Then 5 ml of cupferron solution is added, and the solution is shaken. If the precipitate is white and does not impart a brown color to the chloroform layer in the subsequent extraction the separation is complete; otherwise, further extraction is necessary. A greenish tinge in the chloroform layer, even after complete extraction, is due to excess cupferron.

The aqueous layer is quantitatively transferred from the separatory funnel to the original beaker, and the funnel is washed with two portions of water. Fifteen milliliters of HNO_3 is added, the beaker is covered with a Speedyvap watch glass, the solution is evaporated to heavy fumes of SO_3 , and the fuming is continued for 3 to 5 min. When cooled, the watch glass and sides of the beaker are washed down with at least 15 ml of water. One milliliter of HClO_4 is added, and the solution is again heated to fumes of SO_3 , cooled, and washed down as before. Four fumings are necessary to remove nitrates and organic material. Following the final fuming the sample is cooled, 50 to 75 ml of water is added, and the salts are brought into solution by heating. The solution should have a final volume of 50 to 75 ml and an acid concentration of 5 per cent by volume. With high-grade ores the solution is transferred to a 200-ml volumetric flask, and H_2SO_4 is added so that the total H_2SO_4 after dilution will be 5 per cent by volume. The solution is diluted to volume at room temperature, and a suitable aliquot is taken.

The aliquot is heated to boiling and is oxidized by adding drop by drop 2 per cent potassium permanganate until a permanent pink color results. (One or two drops should be sufficient if all organic matter has been removed.) The solution is rapidly cooled to room temperature by using an ice bath. It is then passed through a Jones reductor, which has been previously washed with 5 per cent H_2SO_4 followed by water, at the rate of 30 to 40 ml per minute. Three 30-ml portions of H_2SO_4 (1 to 19) followed by three 30-ml portions of water are used as wash solution.

The reduced solution is transferred to a 600-ml beaker and aerated for 15 min. The watch glass, aerator, and sides of the beaker are carefully washed down with water. Twenty milliliters of a freshly prepared solution of 4 per cent ferric chloride is added, the solution is thoroughly stirred, and 15 ml of sulfuric-phosphoric acid mixture (350 ml of 85 per cent H_3PO_4 plus 150 ml of H_2SO_4) is added. Eight

drops of sodium diphenylamine sulfonate indicator (0.32 g of barium diphenylamine sulfonate is dissolved in 90 ml of water, 0.5 g of anhydrous sodium sulfate is added, and the solution is stirred, allowed to stand overnight, filtered, and diluted to 100 ml) are added, and the solution is immediately titrated to a permanent purple color with 0.027N potassium dichromate solution.

The titer of the potassium dichromate solution is obtained by dissolving a weighed portion of standard U_3O_8 (MS-ST, 99.95 per cent U_3O_8) in nitric and sulfuric acids and fuming four times to remove the nitrates prior to reduction.

(c) Cupferron-Ceric Sulfate Method.⁴⁵⁴ This method is applicable to ores that are decomposed by treatment with nitric and sulfuric acids. After the insoluble matter has been removed by filtering and washing, the solution is oxidized with potassium permanganate, and iron and other cupferrates are removed by a chloroform extraction. The organic matter in the aqueous layer is then destroyed, and the cooled solution is shaken with liquid zinc amalgam to reduce uranium to the quadrivalent state. The titration is made with ceric sulfate, which may be 0.1N, 0.05N, or 0.02N, depending on the U_3O_8 content; 1,10-phenanthroline ferrous sulfate is used as the indicator.

Procedure.⁴⁵⁴ A 1- to 4-g sample of dried ore, sufficient to contain the uranium equivalent of 30 to 50 ml of the standard ceric solution, is weighed into a 250-ml beaker and digested with 15 ml of HNO_3 and 10 ml of H_2SO_4 until heavy fumes of sulfur trioxide begin to form. When it is cooled the solution is diluted with 50 ml of water and is digested slightly below the boiling point for a few minutes; the hot solution is filtered into a 400-ml beaker. The residue is discarded after it has been thoroughly washed with hot H_2SO_4 (1 to 200). The combined filtrate and washings are concentrated to approximately 50 ml, and the hot solution is treated with a 0.2 per cent potassium permanganate solution until a permanent pink color results.

The solution is cooled in an ice bath and transferred to a 250-ml separatory funnel; sufficient cold water is used as a wash to bring the total volume to approximately 100 ml. After the solution has been made uniform, 15 ml of cold aqueous 5 per cent cupferron solution is added, and the separatory funnel is shaken thoroughly. The resulting mixture is extracted with successive 25-ml portions of chloroform until the chloroform remains colorless. The extracts are discarded. Five milliliters of aqueous cupferron is added to the solution that remains in the separatory funnel. A fine, perfectly white precipitate should be formed; if the precipitate is at all discolored a second 5-ml portion of cupferron solution is added, the funnel is shaken, and the chloroform extractions are repeated. The solution that remains in

the separatory funnel is then tested again with a 5-ml portion of aqueous cupferron. If the precipitate remains perfectly white the mixture is extracted with chloroform until the extract is colorless; otherwise, the cupferron plus chloroform extractions are repeated until a white precipitate is produced by the addition of a 5-ml portion of aqueous cupferron.

After the excess cupferron has been removed by successive extractions with fresh portions of chloroform, the aqueous solution is quantitatively transferred from the separatory funnel to the 400-ml beaker that it occupied immediately prior to the cupferron treatment. Dissolved and entrained chloroform is carefully driven out by heating the solution on a low-temperature hot plate. When the chloroform has been completely expelled the temperature of the hot plate is increased, and the solution is evaporated to fumes of sulfur trioxide. The solution is allowed to fume strongly for 10 min. When cooled, the fumed solution is diluted with 30 ml of water and warmed gently until the salts, which separated during fuming, have dissolved. To the hot solution is added 5 ml of 0.2 per cent potassium permanganate and the mixture is digested at approximately 75°C for 10 min. If brown manganese oxide is not separated during digestion, or if the permanganate color is completely lost by the solution, the digestion is repeated. Manganese oxide and/or excess permanganate are destroyed by careful addition of small portions of solid sodium sulfite to the hot solution; the solution is heated until sulfur dioxide is no longer evolved.

When the solution has been cooled to room temperature, 5 ml of H_2SO_4 is added, and 0.2 per cent potassium permanganate is added drop by drop, until a permanent pink color results. The solution is quantitatively transferred to a 250-ml separatory funnel, using sufficient ice-cold wash water to bring the total volume to 100 to 110 ml. After 5.0 ml of saturated mercury-zinc liquid amalgam (cf. Sec. 3.3b) is added the separatory funnel is shaken for 5 min, and after the separatory funnel has been inserted the stopcock is carefully opened to release any pressure that may have developed. The stopper is washed thoroughly, and the washings are caught in a 500-ml Erlenmeyer flask.

The separatory funnel and the rubber stopper are inserted into the 125-ml filter flask (Fig. 1.5), which contains 75 ml of 1 per cent H_2SO_4 , so that the stem of the funnel extends into the acid. Pressure is built up in the flask with the aid of the rubber atomizer bulb that is attached to the side arm, the separatory stopcock is carefully opened, and air in the stem is allowed to escape through the solution. A portion of the dilute acid is pumped into the funnel to wash the amalgam.

When the pressure has decreased the amalgam flows into the flask. The stopcock is quickly closed as the last of the amalgam leaves the funnel. If a few drops of amalgam remain in the funnel a little mercury is added, and the resulting dilute amalgam is allowed to flow down while being washed by ascending wash acid. After the amalgam has been separated, the remainder of the wash solution is pumped into the flask, the funnel is separated from the flask, the reduced solution is drained into the 500-ml Erlenmeyer flask mentioned above, and the funnel is washed thoroughly.

After the addition of 30 ml of cold H_2SO_4 , 5 ml of H_3PO_4 , and 2 drops of 0.025M 1,10-phenanthroline ferrous sulfate indicator, the reduced solution is titrated with standard ceric sulfate (0.1N, in 0.5M H_2SO_4 standardized against standard U_3O_8 , MS-ST) or National Bureau of Standards arsenious oxide.

A reagent blank is run through all steps of the procedure.

4.4 Volumetric Determination in Concentrates. Mercury Electrolysis-Cupferron-Dichromate Method. The sample is decomposed with hydrochloric, nitric, and sulfuric acids. The arsenic is removed with hydrobromic acid. Heavy metals are then removed by mercury electrolysis. After the solution is oxidized, interfering elements are removed by a cupferron-chloroform extraction. The organic matter is destroyed, and the solution is reduced in a Jones reductor, aerated, and titrated with potassium dichromate.

Procedure.⁴⁵⁵ A 2-g portion of the sample is weighed into a 500-ml Erlenmeyer flask and boiled with 20 ml of HCl (1 to 1) and 10 ml of HNO_3 (1 to 1). Then 16 ml of H_2SO_4 (1 to 1) is added, and the solution is heated until fumes of sulfur trioxide are evolved. After it is cooled, 20 ml of HBr (1 to 1) and 15 ml of HCl (1 to 1) are added and the solution is heated again to fumes of SO_3 . The treatment with HCl and HBr is repeated as above to complete the removal of the arsenic. When cool, the sides of the flask are washed down with water, 10 ml of HNO_3 is added, and the solution is then heated until SO_3 fumes are evolved. The solution is fumed three times; the sides of the flask are washed down after each fuming. When cooled after the last fuming, the sides of the flask are again washed down with water, and about 90 ml of distilled water is added. The solution is heated to boiling to dissolve all soluble salts and is filtered through a Whatman No. 1 filter paper. The flask and residue are thoroughly washed with hot water. The residue, which contains U_3O_8 to an extent insignificant to the accuracy of the determination, is discarded. The filtrate is boiled down to a volume of 100 ml and cooled to room temperature.

Sufficient mercury is poured into the Melaven electrolytic cell⁴⁵⁶ through the leveling bulb to bring the mercury level in the cell to a

point of maximum surface area. The filtrate is transferred to the cell, and the flask is washed out with 100 ml of water, which is added to the cell. The platinum anode is connected to the positive wire, and the cathode wire is inserted into the mercury column in the leveling bulb. The glass stirrer is inserted so that the blade just breaks the surface of the mercury, and the cell is covered with a split watch glass. The solution is electrolyzed at a current of approximately 5 amp for 1 hr and then at about 2 amp for an additional hour; it is stirred continually.

After electrolysis has been completed, the stirrer is stopped, and the mercury is drained from the cell; a portion of the mercury is left in the stopcock bore. The sample is drained into an 800-ml beaker, the stopcock is closed, cover glass and cell walls are washed down with 200 ml of H_2SO_4 (1 to 49), the mercury is returned to the cell, and the electrolysis is allowed to proceed for 5 min. The wash solution is drained from the cell into the same 800-ml beaker that was used before.

The electrolyzed solution and washings are evaporated to a low volume on the steam bath. Five milliliters of HNO_3 is added and the solution is heated until fumes of SO_3 are evolved. After it is cooled the sample is diluted with water and transferred to a 500-ml Erlenmeyer flask, evaporated to a volume of 100 ml, and oxidized with potassium permanganate solution. Any vanadium that is present is removed by a cupferron extraction. The determination is completed as set forth in the sulfide-cupferron-dichromate method, Sec. 4.3b.

The mercury for the cell must be cleaned after three or four samples have been electrolyzed. The used mercury is placed in a heavy-walled Florence flask supported on a piece of sponge rubber. Air is bubbled through the mercury with 200 ml of HNO_3 (1 to 9) for 3 hr, this acid is discarded, the 100 ml of HNO_3 (1 to 9) is added, and air is bubbled through for 2 hr more. This is followed with another washing with HNO_3 (1 to 9) for another hour, a 2-hr washing with H_2SO_4 (5 to 95), and then with several separate washings with distilled water.

4.5 Colorimetric Determination in Ores. Double Cupferron-Basic Peroxide Method.³⁶³ In this procedure the sample is completely decomposed, and almost all the iron is extracted with ethyl acetate. After reduction the uranium is precipitated with cupferron, along with titanium, vanadium, etc. The cupferrates are ignited, and after oxidation the titanium, vanadium, etc., are removed by extraction of the cupferrates. The uranium in the solution is determined by the sodium hydroxide-sodium peroxide colorimetric method.

With ores that contain heavy metals, it may be necessary to pretreat the solution with zinc or with hydrogen sulfide to avoid the pre-

precipitation of these elements in the reductor. The solution to be passed through the reductor should have as small a volume as is consistent with solution of the salts and should contain approximately 10 per cent hydrochloric acid by volume. The cupferron precipitation is conducted in solutions of hydrochloric acid 4 to 8 per cent by volume. Perchlorate and sulfate do not interfere.

Procedure.³⁶³ A 5-g sample (for samples with a total radioactivity count equivalent to 0.015 per cent uranium or less) ground to pass 60- to 80-mesh screen is weighed. If the sample contains organic matter or sulfides it is ignited at top heat of a Meker or Fisher burner. It is then digested in a covered platinum dish on the steam bath for 30 min with 40 ml of HNO_3 (1 to 1). The cover is removed, 10 to 15 ml of HF is added, and the solution is slowly evaporated to dryness on a steam bath. If there is much unattacked material the digestion with acid is repeated. The sample is then evaporated to dryness twice with HNO_3 . The dry residue is transferred to a porcelain or glass container, the platinum dish is rinsed with HCl (1 to 1), 10 ml of HCl is added, and the solution is evaporated to dryness. This is followed by two more evaporations to dryness with HCl. The residue is digested, while covered, with 20 ml of HCl (1 to 1), the solution is filtered, and the residue is washed with hot HCl (1 to 1) and finally with a little hot water. The residue is then ignited in platinum a little HF and 1 drop of H_2SO_4 are added, and the solution is evaporated to dryness. The remaining residue is sintered with as little Na_2CO_3 as possible and is dissolved in HCl (1 to 1). If there is any unattacked residue, it is filtered and sintered with Na_2CO_3 and dissolved in HCl (1 to 1).

If much SiO_2 separates, the fusion mixture is treated with HCl (1 to 1), evaporated to dryness in platinum, treated with HF and a few drops of H_2SO_4 , and fumed. This residue is then taken up in HCl (1 to 1) and added to the main sample. If little or no SiO_2 separates when the fusion mixture is treated with HCl (1 to 1), the solution is added to the previous filtrates. The combined filtrates are evaporated to about 25 ml. If there is any residue it is filtered off and dissolved in hot water, and this solution is added to the main portions after the iron extraction.

Iron is removed by two extractions with 50 to 100 ml of ethyl acetate, and the ethyl acetate layers are rejected. The combined water layers from the extraction of iron are evaporated to dryness, 10 ml of HCl (1 to 1) is added, and the solution is digested on the steam bath for 15 min. Twenty milliliters of water is added, and the digestion is continued until the soluble salts dissolve. Insolubles are filtered off and washed with water, and the residues are rejected.

The solution, 50 ml in volume, is passed through a zinc reductor (10 to 12 in. long and of about $\frac{1}{2}$ in. bore) that is amalgamated with 3 or 10 per cent by weight of mercury. The 10 per cent amalgam is used for samples that contain nickel. The solution is collected directly into 15 ml of 6 per cent cupferron solution contained in a 125-ml Erlenmeyer flask immersed in an ice bath; the flask is shaken during the passage. The reductor column is washed with 10 ml of 5 per cent HCl and then with enough water to make the contents of the flask 100 ml.

The flask with its contents is allowed to stand in the ice bath for about 5 min and is stirred occasionally. A little paper pulp is mixed in and the precipitate is filtered off. Washing is accomplished with cold 6 per cent HCl that contains 1.5 g of cupferron per liter.

The cupferron precipitate is burned in porcelain. The ignition is started at low heat until the paper is carbonized, and then the heat is increased until the carbon is burned off. The final temperature should be about 750°C. The residue is fused with a little potassium pyrosulfate. The melt is kept in quiet fusion until the residue is dissolved and any carbon that might be present owing to faulty ignition of the cupferron precipitate is also gone. The melt is allowed to cool; then it is dissolved in 50 ml of water that contains 4.5 ml of HCl.

The solution is passed through the reductor and precipitated as before. The second reduction is not necessary if the solution, before the first passage through the reductor, showed no visible green chromium color.

The second ignited cupferron precipitate is fused with potassium pyrosulfate as before. After it has cooled somewhat, 10 to 25 mg of NaNO_3 is added, and the fusion is continued until the nitrate is gone. The melt is cooled and dissolved in 30 ml of water containing 3.5 ml of HCl and is then cooled in an ice bath.

The solution is transferred to a separatory funnel. Fifteen milliliters of cold 6 per cent cupferron solution is added, and the solution is shaken several times. Thirty milliliters of cold ethyl acetate is added, the mixture is shaken and allowed to settle, and the layers are separated. Two more extractions of the water layer with ethyl acetate are made. The ethyl acetate layers are rejected.

The water layer is evaporated to a small volume. Fifteen milliliters of HNO_3 is added, and the solution is evaporated to dryness. One milliliter of H_2SO_4 is added, and the sample is covered with a watch glass and fumed gently on the hot plate. The last trace of organic matter is destroyed by cautious drop-by-drop addition of 1 ml of fuming HNO_3 . The HNO_3 is introduced by a pipet that is inserted under the cover glass and directed against the side of the beaker. The

sample is allowed to fume for 5 min after the HNO_3 is gone. The treatment with HNO_3 is repeated, and again the sample is allowed to fume for 5 min after the HNO_3 has been removed. After the sample has cooled 35 ml of water is added, and the mixture is boiled gently to obtain solution. (Sometimes double sulfates of rare earths and potassium precipitate, but they are not filtered until the hydroxide solution is filtered.) The solution is cooled to about 50°C , 6 drops of 30 per cent hydrogen peroxide is added; then 50 per cent NaOH is added drop by drop until neutral, with 1 ml in excess. After it has cooled again, the volume of the solution is made to 50 ml in a graduated cylinder. The solution is filtered through a 7-cm Whatman No. 40 filter paper but it is not washed.

The solution is compared visually with solutions that contain known quantities of uranium. These solutions of uranium are made up to 50-ml volume and contain 1 ml of 50 per cent NaOH and 6 drops of 30 per cent H_2O_2 . The comparison is conveniently made in Nessler tubes.

4.6 Colorimetric Determination in Sodium Vanadate. Calcium Hydroxide-Basic Peroxide Method. In this procedure calcium hydroxide is used to gather the uranium, and the uranium is determined colorimetrically by the sodium hydroxide-sodium peroxide method, which eliminates interference from vanadium.

Procedure.³⁷⁶ A 10-g sample is placed in a 600-ml beaker and 30 ml of 50 per cent NaOH solution and 300 ml of H_2O are added. A few glass beads are added, the beaker is covered, and the solution is boiled vigorously until the volume is about 100 ml. About 300 ml of water is added, and the solution is heated to boiling. Then it is removed from the hot plate, and 10 ml of a calcium nitrate solution [1.2 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per 100 ml] is added. The precipitate is allowed to settle and is filtered through a Whatman No. 40 filter paper.

The filter paper and contents are transferred to the original beaker, 20 ml of HNO_3 (1 to 1) is added, and the solution is heated until the precipitate on the filter paper is in solution. About 100 ml of water is added, the mixture is heated a few minutes, and then it is filtered through a Whatman No. 1 filter paper and washed with hot water.

To the filtrate are added a few glass beads and 3 ml of H_2SO_4 . The solution is evaporated to fumes of SO_3 and then cooled. The sides of the flask are washed with water, the acid is neutralized with 50 per cent NaOH solution, 20 ml in excess is added, and the total volume is brought up to 100 ml. One-half gram of Na_2O_2 is added, and the solution is filtered through a double Whatman No. 1 filter paper into a dry 250-ml Erlenmeyer flask until about 40 ml of the filtrate has been collected. An additional 0.5 g of Na_2O_2 is added, the flask is covered with a small watch glass, and the solution is brought just to a boil.

After the solution has been allowed to cool slowly to room temperature, the transmittancy is measured at $425\text{ m}\mu$. The uranium concentration is obtained from a previously prepared transmittancy-concentration curve made under the same conditions.

4.7 Colorimetric Determination in Monazite Sands. Ammonium Hydroxide-Ether-Basic Peroxide Method.¹⁷² Samples of 2 to 5 g are decomposed with potassium bifluoride and sulfuric acid. Samples of less than 2 g can be handled when brought into solution by heating with sulfuric acid. After the sulfate ion has been removed by ammonium hydroxide precipitation the sample is converted to nitrate, and an ether extraction is made after saturation with ammonium nitrate, ferric nitrate being used to complex the phosphate ion. The uranium content of the extract is determined by the sodium hydroxide-sodium peroxide colorimetric method. Other ores are analyzed by the same general procedure following suitable decomposition. With ores containing less than 0.005 per cent U_3O_8 , the ether extract is generally analyzed by fluorescence methods as given in Sec. 3.

Procedure.¹⁷² The sample of 3 to 5 g is placed in a platinum crucible, mixed with twice its weight of potassium bifluoride, and heated over a low flame until the fusion mass partially solidifies. It is then heated more strongly until a clear melt is obtained. After it has cooled, the melt is removed from the crucible and digested in a 200-ml platinum dish with about 75 ml of water and 15 to 20 ml of H_2SO_4 ; any lumps are crushed with a bakelite or platinum rod. After the melt has disintegrated, the solution is evaporated on the steam bath and is then heated on a hot plate until SO_3 fumes are evolved. The fuming is continued for about 5 min, and care is taken to bring the fuming acid in contact with any residue on the sides of the dish. After it has cooled, the residue is transferred to a beaker, about 300 ml of H_2O is added, and the solution is allowed to digest until all the lumps have broken up. The solution is then filtered, and the residue is washed with hot water and discarded.

The filtrate is heated to boiling, and the R_2O_3 group is precipitated with carbonate-free NH_4OH . The precipitate is digested for a few minutes at a temperature just below boiling and is then filtered; the residue is not washed. The precipitate is dissolved on the paper with hot HNO_3 (1 to 9), and the solution is caught in the original beaker. At least two more NH_4OH precipitations are required to remove sulfates that interfere with the ether extraction.

The last HNO_3 solution is evaporated almost to dryness, and the residue is dissolved in 20 ml of HNO_3 (1 to 3). If not clear, this solution is filtered through a small Whatman No. 40 filter paper, and the residue is washed with 30 ml of HNO_3 (1 to 5), thus bringing the final

volume to 50 ml. Sodium nitrite (0.5 g) is added to reduce cerium so that it will not be extracted. Ten grams of ferric nitrate is added to the solution, which is then saturated with ammonium nitrate preparatory to the ether extraction.

The nitrate solution is transferred to a continuous extractor (Fig. 1.1) and extracted for 1 hr. After 30 min, 5 ml of HNO_3 saturated with NH_4NO_3 is added through the small side opening, and the extraction is continued for an additional 30 min. During the extraction the aqueous layer is stirred every 10 min by raising the condenser and moving the frit up and down.

The water and ether layers that contain the uranium are transferred from the collection flask of the extractor to a 250-ml beaker, and the ether is evaporated on the steam bath; 2 to 3 ml of H_2SO_4 is added, and the solution is evaporated to fumes of SO_3 in a covered beaker that contains a few glass beads. The beaker is kept in motion to prevent spattering when the volume gets low. After the solution has cooled, the cover and sides of the beaker are washed down with a small volume of water, 3 ml of HNO_3 and 3 ml of HClO_4 are added, and the solution is again evaporated to fumes of SO_3 . After the solution has cooled, the sides of the beaker and cover are again washed down with water, the acid is neutralized with NaOH (1 to 1), and approximately 1 g of Na_2O_2 is added. From the color produced it is determined what the final volume should be (usually 50 to 100 ml), NaOH (1 to 1) amounting to 5 per cent of the final volume is added, and the solution is diluted to that volume with water. The solution is filtered through a double Whatman No. 1 filter paper into a dry container, and the transmittancy is measured at 425 $\text{m}\mu$ on a Coleman 10S (5- $\text{m}\mu$ slit) spectrophotometer using 1.8-cm cylindrical cells.

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Chapter 2

THORIUM

By C. J. Rodden and J. C. Warf

In this chapter the general chemistry of thorium is briefly discussed with the greatest emphasis on analytical chemistry. Other sources of collected information on thorium are listed in the bibliography.¹⁻⁷

In general, the analytical chemistry is not so complicated and is not so fully developed as in the case of uranium. The methods of separating thorium are discussed at some length; these include precipitation, formation of various complexes, and volatilization.

The determination of thorium by gravimetric, titrimetric, and colorimetric means is discussed.

1. THE CHEMISTRY OF THORIUM AND ITS COMPOUNDS

Thorium-bearing minerals are found on all continents and major islands although usually in negligibly small deposits. Monazite, the principal source, is found in reasonably large deposits in India and South America. Monazite is a heavy mineral and occurs admixed with various types of sand. It is dark and has an iridescent purple luster. Monazite is a mixed phosphate of thorium and the rare earths but contains variable amounts of siliceous matter, iron, aluminum, magnesium, and smaller quantities of many other elements. Typical samples contain about 4 per cent thorium. Thorite, a silicate, and thorianite, an oxide that contains uranium and the rare earths, are two of the less important sources.

There are several metallurgical processes for the preparation of metallic thorium. Three of the most successful procedures are as follows: Small quantities of moderately pure metal may be prepared from the thermal decomposition of the vapor of a thorium halide (i.e., ThF_4) on an electrically heated filament (i.e., tungsten). Scales of a rather impure pyrophoric product are obtained by the electrolysis of

a molten potassium fluoride solution of thorium fluoride. It may be prepared by the reduction of thoria (ThO_2) with calcium; the calcium oxide formed is leached away, and the resulting thorium powder is dried and sintered to massive metal. The samples prepared by this method contain 0.5 to 2 per cent thorium dioxide.

Thorium is a silvery-white metal whose physical properties are greatly influenced by the degree of contamination with its oxide. The purest specimens contain several tenths of a per cent of ThO_2 , which may be in solid solution with the metal as such or possibly as a lower oxide. Samples low in oxide tarnish slowly in air, becoming gray, and eventually black, whereas those high in oxide (1.5 to 2 per cent ThO_2) are apparently air-stable and maintain a silvery brilliance for months. The density of the metal is also influenced by the oxide content; the values for various samples range from 11.4 to 11.7. The fact that numerous values have been reported for the melting point of thorium (most are in the range 1800 to 1850°C) can probably be ascribed to variable oxide content; the higher the proportion of oxide, the higher the melting point. Reliable data on the melting point are still lacking, but it is probably between 1650 and 1750°C. The hardness of thorium also varies with the oxide content—the purer specimens are rather soft (Rockwell E hardness of about 65) and are comparable to a soft yellow brass. The samples with the greater amounts of oxide are harder (Rockwell E hardness of 80 to 100) and approach nickel in hardness.

Thorium forms alloys readily. Numerous intermetallic compounds have been prepared. The metal is only slightly soluble in mercury but forms at least one intermetallic compound with this element.

The massive metal is only slowly attacked by water and is smoothly converted to thoria by superheated steam at 850°C. The metal does not dissolve rapidly in any of the common acids except hydrochloric, but several other solution methods are known (see Sec. 2). When heated in air, thorium turnings ignite and burn brilliantly, emitting white light, but ignition in a muffle at 1000°C is necessary to ensure complete conversion to the oxide; massive metal is more slowly converted to the oxide by this treatment. Powdered preparations are often pyrophoric. The heated metal reacts with chlorine, bromine, hydrogen sulfide, nitrogen, hydrogen, and other materials. Thorium forms many types of compounds, some of which are briefly described in the following paragraphs.

Thorium reacts with hydrogen at 450 to 500°C to form a lower hydride, ThH_2 , and a higher hydride, $\text{ThH}_{3.75}$ or ThH_4 . As with uranium hydride, thorium hydride serves as the starting point for the synthesis of a series of other compounds. The thorium hydrides react

with hydrogen chloride, bromide, sulfide, etc., and form the chloride, bromide, sulfide, etc.; this action parallels the behavior of uranium hydride.

The common oxide of thorium is ThO_2 . Peroxides that contain anions are also known. The dioxide is prepared by igniting the hydroxide, nitrate, sulfate, or the salt of an organic acid. It is a white powder whose properties depend on the source and temperature of formation. The nitrate yields a light voluminous powder, but the sulfate gives a much denser product. It has been called the most refractory substance known. The hydroxide, $\text{Th}(\text{OH})_4$, is precipitated as a gelatinous white mass when an alkali hydroxide or ammonia is added to a solution of a thorium salt. It is readily soluble in acids, forming salts, and in solutions of alkali carbonates, forming complex carbonates.

Thorium nitrate is probably the most common salt. It forms several hydrates ranging up to 12 molecules of water of hydration. The nitrate is readily prepared by dissolving the hydroxide or carbonate in nitric acid.

The phosphates of thorium are important, being used in the separation from monazite sand. The normal phosphate, $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, is precipitated by sodium phosphate. A pyrophosphate, $\text{ThP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, is precipitated by sodium pyrophosphate. The phosphates are difficult to dissolve in dilute acids.

Thorium fluoride is precipitated as $\text{ThF}_4 \cdot 8\text{H}_2\text{O}$ when HF is added to a solution of a thorium salt. The chloride and bromide are formed as readily soluble hydrates. All the halides are completely hydrolyzed by steam.

Thorium iodate is insoluble in strong acid and is useful in making separations because the rare-earth iodates are soluble.

Thorium oxalate, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$, is precipitated in an acid solution. It is soluble in ammonium carbonate and ammonium oxalate.

One of the most characteristic features of thorium is its tendency to form double salts; examples are



Other important compounds include the acetate, the salts of a number of organic acids, the basic carbonate $\text{ThOCO}_3 \cdot 8\text{H}_2\text{O}$, and the ferrocyanide. The solution chemistry of thorium greatly resembles that of other quadrivalent cations, notably the uranium(IV) and cerium(IV) ions, but differs from these in that it has only a single valence state.

Thorium forms a wide variety of complex compounds; its coordination number is generally 6 or 8. The double salts mentioned above [K_2ThF_6 , $(NH_4)_4Th(C_2O_4)_4$, etc.] may be put in this category. Chelate complexes are formed with carbonates, oxalates, tartrates, citrates, salicylates, cupferron, oxine, and other organic compounds; some of these have important analytical applications.

The spectrum of thorium is nearly as complex as that of uranium, but satisfactory spectrochemical analyses may be made using thoria as the refractory matrix material by the carrier-distillation technique which is in common use with uranium.

In contrast to uranium, thorium compounds in a fused sodium fluoride bead show only a faint yellow fluorescence when exposed to ultraviolet light. A weak fluorescence is shown by the thorium derivatives of certain dyes when their slightly acid solutions are employed.

The solution chemistry of thorium is that of a typical heavy metal. It is more electropositive than most other such metals, being comparable to magnesium. The colorless nature of the ion and its single valence state render its analytical chemistry more difficult than that of uranium. Thorium salts are stable in aqueous solution and are only slightly hydrolyzed; the pH of a 0.01M thorium nitrate solution is 3.6, and it is at this pH that thorium hydroxide begins to precipitate when thorium solutions are made alkaline. Several reagents form complexes with thorium salts, some of which are stable in alkaline solution, others in strongly acid solution. No reduction to the metal occurs when thorium salts are electrolyzed.

2. METHODS OF SOLUTION

Thorium metal is rapidly attacked by hydrochloric acid (6N to 12N), forming thorium chloride. A gray insoluble residue remains when most metallic thorium preparations are so treated; this represents the oxide that was originally present in the metal. It is gray because of its elementary thorium content, and on long boiling with hydrochloric acid it slowly becomes lighter. Dilute sulfuric acid scarcely attacks thorium.

Nitric acid, dilute or concentrated, hot or cold, passifies the surface of massive thorium, and the rate of solution is prohibitively low. It has been found, however, that traces (0.01M to 0.03M) of the fluoride ion exert an extraordinary catalytic influence and cause the thorium to dissolve rapidly.^{8,9} This effect is not confined to thorium metal but is manifested in the solution of thorium oxide (and other oxides, e.g., ceria), thorium alloys, and insoluble thorium compounds in general. The residue that remains after thorium is treated with

hydrochloric acid may also be caused to dissolve by adding a little fluoride ion, but the effect is less pronounced here. The fluoride may be added as hydrofluoric acid or sodium fluoride, but if glassware rather than platinum ware is in use it should be added as fluosilicic acid or sodium or ammonium fluosilicate to avoid etching. The nitric acid concentration should be 8N to 16N. When large quantities of thorium turnings (100 to 500 g) are to be dissolved, they must be added gradually to prevent the reaction from getting out of control.

Perchloric acid does not attack thorium when dilute, and it acts very slowly on the massive metal when hot and concentrated; the latter treatment may become dangerous with samples of large surface area. Fuming with phosphoric acid slowly but completely dissolves thorium. Fusion of small samples with potassium acid sulfate attacks the metal and permits complete solution.¹⁰ Thorium may be converted to thoria by oxidation with superheated steam at 850 to 900°C and then dissolved as usual.¹¹

The reaction of thorium dioxide toward solution reagents depends on its previous heat-treatment. Low-burned oxide that is heated not over 550 to 600°C generally dissolves readily in acids; oxide heated to higher temperatures becomes increasingly difficult to dissolve. Hot nitric acid, approximately 0.03M in fluoride, dissolves all types of thoria, but those that were previously heated to high temperatures require the longest times. Hydrochloric acid-fluoride mixtures are even less effective toward the high-burned preparations. Fusion of thoria with sodium acid sulfate or pyrosulfate, or sodium pyrophosphate, also yields a water- or acid-soluble derivative.

Thorium fluoride is dissolved slowly by fuming with sulfuric acid or by long fuming with perchloric acid. It is also responsive toward thorium-complexing agents, notably the alkali oxalates, and the fluoride-complexing agents, notably boric acid. Specimens that have been sintered or fused are only slowly dissolved. An alternative procedure involves pyrohydrolysis to the oxide to expel the fluorine¹² followed by solution by the ordinary methods. The solution of ores and minerals will vary considerably and a series of treatments may be necessary.¹³

3. METHODS OF SEPARATION

It is impossible to evaluate the various methods as applied to all materials. In some samples of simple hydroxide, precipitation would serve the purpose whereas in others, for example in ores, a rather laborious and time-consuming operation is necessary.

The precipitation of thorium oxalate with oxalic acid is one of the most commonly used methods, and it is satisfactory for most pur-

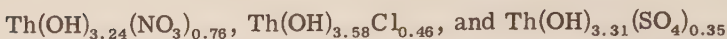
poses. A separation from the rare-earth elements is not made. The solubility of the oxalate is such, however, that for traces it is not applicable. Thorium fluoride has been used for years as a method of separating thorium from other interfering substances. It is especially useful in the separation from zirconium. Its chief disadvantage is that it affords no separation from the rare-earth elements. Thorium iodate in strong acid solution separates thorium from the rare earths. Its chief disadvantage is that several precipitations are usually required, and other elements, such as zirconium and ceric cerium, are also precipitated. The separation of thorium as the peroxide shows promise of shortening some of the more laborious procedures now used, especially where many interfering elements are present, as in minerals and ores.

Organic reagents are not of general use in the separation of thorium, except in so far as the thorium occurs in an alloy with another element that is not precipitated by the organic compound. There are so many other elements that would come down with thorium with the usual organic reagents used for this element that they are of little or no value. Complexes of thorium with carbonate, such as are found useful in the uranium separations, are not widely employed. The usual citrate and tartrate complexes are sometimes used to hold the thorium in alkaline solutions. Extraction procedures as applied to analytical methods have not been widely employed.

As may be seen from the above discussion, the only method of separation used to any extent is precipitation. Precipitation methods are considered in detail in the following section, even though they may not be applicable except in certain specific cases owing to the presence of other interfering elements.

3.1 Precipitation. Nearly all the analytically useful methods of precipitation for thorium are outlined below. Most of the separations from other elements which are achieved by these procedures have been incompletely studied. Some of the precipitates are soluble in organic solvents and may be useful in extraction procedures.

(a) **Thorium Hydroxide.** When alkalis are added to thorium solutions a flocculent, gelatinous precipitate of thorium hydroxide is formed. The precipitation is quantitative, and the white, voluminous hydroxide does not dissolve to any extent in an excess of the alkali. The pH of 3.5 to 3.6 at which the precipitation begins is nearly independent of the thorium concentration. The first precipitate to form is not the pure hydroxide, but it carries down some of the anion as a basic salt; there is too much of the anion to be accounted for by mere adsorption.¹⁴ Typical precipitates correspond approximately to the compositions



When freshly precipitated the hydroxide dissolves readily in acids, but if it is permitted to stand several hours, or if it is dried, it becomes more acid-resistant. This may be attributable to the conversion of the hydroxide into a hydrated oxide. On drying, the hydroxide shrinks a great deal and becomes hard and glassy.

Ammonium hydroxide is generally used for the precipitation, and, because carbonates complex thorium, a carbonate-free reagent must be employed in the most accurate work. The other common thorium-complexing ions must also be absent. These include tartaric and other hydroxy acids, sugars, glycerol, etc.^{15,16}

Separations are made from those ions that are not precipitated by ammonia. Thus when an excess of ammonium salts is present, separations are made from the alkali metals, the alkaline earths, zinc, nickel, copper, silver, and other metals; in some of these, multiple precipitations are necessary. Separation from tungsten is effected,¹⁷ but uranium is precipitated as well as most other heavy metals. The precipitation of ferric hydroxide may be employed to carry traces of thorium hydroxide.¹⁸ Colloidal suspensions of thorium hydroxide have been prepared.¹⁹

The separation of thorium from the rare earths is a problem that has received detailed attention, and several methods of precipitating thorium hydroxide without precipitating the rare-earth hydroxides have been employed. Potassium azide effects this separation, and when a thorium solution is boiled with this reagent the reagent is hydrolyzed, thorium hydroxide is precipitated quantitatively, and hydrazoic acid is boiled away.²⁰ This method is seldom used at the present time. Sodium thiosulfate accomplishes the same end, but one or more reprecipitations are required for complete separation from cerium; only a partial separation from uranium is made.^{21,22} Aluminum, scandium, titanium, and zirconium are also precipitated. Hexamethylenetetramine is a third reagent that causes the preferential precipitation of thorium hydroxide and separates it from the rare earths.^{23,25} Still another reagent is pyridine.²⁴ When present in large amounts the rare earths may precipitate partially. The thiosulfate procedure has been used for years as an analytical method.

Procedure (Ammonium Hydroxide). The thorium solution, which usually contains 10 to 150 mg of thorium and is free of tartrates, etc., is treated with ammonium hydroxide (1 to 9) with stirring until the mineral acids are nearly neutralized. If no mineral acid is present, 2 or 3 g of ammonium nitrate is added. The slightly acid solution is

heated to boiling, and ammonium hydroxide is added until the solution smells strongly of ammonia (pH 9 to 11). The gelatinous precipitate is filtered off and washed several times with a 2 per cent ammonium nitrate solution made basic with ammonia.

Procedure (Potassium Azide).²⁰ The thorium solution is treated with ammonia until it is only slightly acid (pH 2.5 to 3) and is then boiled 5 min in a hood with an excess of potassium or sodium azide. Before addition of the azide, any quadrivalent cerium is reduced with hydrogen peroxide, the excess of which is destroyed by boiling. The precipitate is filtered and washed as above.

Procedure (Sodium Thiosulfate).⁶ The chloride solution, containing not more than 0.2 to 0.3 g of thoria, is evaporated to dryness on the water bath; the residue is moistened with water, dried again, and then dissolved in 200 ml of hot water; after it has cooled, the resulting solution is treated with 5 g of sodium thiosulfate and heated slowly to 80–90°C with occasional stirring. The beaker is placed on the water bath, and the precipitate is allowed to settle for 30 min; then it is filtered on a Whatman No. 41 filter paper, washed with warm water, and returned to the beaker with a minimum of hot water; 5 ml of hydrochloric acid is added, the mixture is boiled to dissolve the thoria, and the solution is filtered through the same paper to remove the sulfur. The filtrate is collected in a 200-ml glass dish and evaporated to dryness on the water bath. The thoria is then reprecipitated as before except that only 3 g of thiosulfate is required; after one more repetition of the whole process the thoria precipitate is free from rare earths. This third precipitate is extracted with 5 ml of hydrochloric acid, and the thorium in the filtered solution is precipitated as oxalate. The three filtrates from the thiosulfate precipitates are combined and boiled for 1 hr; any small precipitate thus produced is collected and ignited together with the three sulfur residues. The resulting oxides are dissolved by fusion with a small piece of potassium bisulfate in a silver crucible, the melt is dissolved in hot water, the unfiltered solution is boiled with a slight excess of sodium hydroxide, and the washed precipitate is dissolved in hydrochloric acid; this solution is evaporated, and any small amount of thoria contained therein is recovered by boiling with thiosulfate. The precipitate is usually very small; therefore, it is sufficient to extract it with a few milliliters of hydrochloric acid and to precipitate the thoria in the filtered extract by addition of oxalic acid, keeping the volume as low as possible.

Procedure (Hexamethylenetetramine).²³ The chloride solution is cautiously treated with ammonium hydroxide (1 to 10) until a faint permanent turbidity is produced, which is cleared by the addition of

a few drops of hydrochloric acid (1 to 1); the solution is diluted to 200 ml, treated with 10 g of ammonium chloride, and heated to 70 to 80°C; the thorium is precipitated by the slow addition of a 2 per cent solution of hexamine until no further turbidity is produced. The precipitate is collected on a filter paper, washed with warm 5 per cent ammonium chloride solution, returned to the beaker, and dissolved by the addition of a few drops of hydrochloric acid. The solution is neutralized, diluted, and treated with ammonium chloride and hexamine as before; a third precipitation is advisable if a considerable amount of rare earths is present. The final hexamine precipitate is dissolved in hydrochloric acid, and the thorium is precipitated as oxalate. Zirconia and titania accompany the thorium in the hexamine process, but they are eliminated by the oxalate precipitation.

(b) Thorium Peroxide. The older literature¹ gives thorium peroxide variously as Th_2O_7 and ThO_3 when it is precipitated by hydrogen peroxide from mildly acid solutions in the presence of ammonium salts. More recent studies^{26,27} indicate that there are two types of thorium peroxides, and both contain anions. The first, precipitated from weakly acid or ammoniacal medium, forms a very poorly crystalline substance of variable composition that contains anions such as nitrate, chloride, or perchlorate and water of crystallization. The second type is evidently an entirely different type of compound and is formed primarily as the sulfate. It has a definite composition, $\text{ThOOSO}_4 \cdot 3\text{H}_2\text{O}$, and is called "thorium peroxide sulfate."

The peroxide content and physical nature of the first type vary widely with the precipitation conditions. From a neutral solution the peroxide is gelatinous and has a tendency to be transparent, from a slightly basic solution it is not so gelatinous and has a lower peroxide content, and from acid solutions it is most nearly completely precipitated at elevated temperatures, is opaque, and is more readily filtered. Thorium peroxide sulfate, on the contrary, is dense and crystalline and forms from a hot sulfuric acid solution. If precipitated from a too weakly acid solution, the product is of the same nature as the less crystalline variety, e.g., thorium peroxide nitrate.

Although separations have been made in ammoniacal solutions, separations from the ammonium hydroxide groups are not made, and the method is of little value. In neutral or acid mediums, separations are made from the alkali metals, boron, beryllium, and magnesium.²⁸ Fair separations are made from the rare earths, but cerium may follow in small amounts, and no separation is made from zirconium and titanium. Precipitation in acid has been used for rapid analysis of monazite sands.²⁹

Procedure (from Ammoniacal Solution).²⁶ The thorium nitrate, chloride, or perchlorate solution containing 10 to 30 mg of thorium per 50 ml is adjusted to pH 2 to 3, and a large excess of 30 per cent hydrogen peroxide is added. Ammonia is then added for basic precipitations. The solution is cooled to 0°C and is allowed to stand for an hour or more. It is then filtered and washed with cold water.

Procedure (from Neutral Solution).³⁰ The neutral solution of the nitrates of thorium, cerium, and lanthanum is treated with 10 g of ammonium nitrate. The solution is diluted to 100 ml and warmed to 60 to 80°C, and the thorium is precipitated by adding 20 ml of 3 per cent hydrogen peroxide. The precipitate is filtered and washed with a hot 2 per cent solution of ammonium nitrate.

Procedure (from Acid Solution).²⁹ To the acid solution hydrogen peroxide is added in excess; the pH is adjusted to 0.5 to 1.5 by using ammonium hydroxide and/or nitric acid. The mixture is warmed to 50 to 60°C, and the compact precipitate is filtered and washed with 2 per cent ammonium nitrate solution.

Procedure (from Sulfate Solution). The thorium solution, containing 10 to 30 mg of thorium per 50 ml, is adjusted to 1N to 2N in sulfuric acid. Since acid is formed by the reaction, as in the case of uranium, the initial hydrogen-ion concentration should be lower for those samples that are high in thorium. The final acid concentration should not exceed 2N. An excess of 30 per cent hydrogen peroxide is added, and the mixture is stirred, heated to 55 to 60°C, and allowed to cool to room temperature. After standing an hour or more the $\text{ThO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ is filtered and washed with water.

(c) Thorium Oxalate. The separation of thorium as the oxalate is a classic method and is widely employed. In the common gravimetric procedures for thorium the oxalate is precipitated and ignited to the oxide. The oxalate precipitation method is frequently used because it can be carried out in acid solution, and thorium is thus separated from many other elements. Thorium oxalate precipitates may be either crystalline and readily filtered or nearly gelatinous, slimy, and difficultly filterable, depending on conditions.^{6, 22, 31} The temperature, rate of precipitation, and acidity affect the nature of the precipitate. The greater the acidity, the denser the precipitate; a given amount of thorium oxalate precipitated from 1.5N acid is only about half as voluminous as the same amount precipitated from a 0.5N acid solution.³² Excessive acid concentrations prevent quantitative precipitation, but by adding an excess of oxalic acid complete recoveries can be effected in 1N to 2N acid. As ordinarily formed the oxalate is the hexahydrate, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.

Separations from most elements other than the rare earths are achieved by the oxalate precipitation. The oxalates of metals such as calcium, strontium, barium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, and bismuth are more or less insoluble in neutral solution but soluble in acid solution. When present in large amounts, they may contaminate the thorium oxalate and render preliminary separations by another method or double precipitations necessary. Thus thorium oxalate precipitated from 1N to 2N nitric acid solutions that were 0.2M to 0.3M in calcium contained about 0.2 per cent calcium.³¹ Zirconium has a tendency to precipitate with the thorium but can be kept in solution with an excess of oxalate. Enough oxalate must be added to satisfy the oxalate-complexing ions, uranyl and ferric. The uranyl oxalate complex may be reduced by photochemical action, and some uranous oxalate may precipitate; however, this is not serious, and good separations are made. Oxalate also reduces metals, such as gold, that may precipitate as the free metals. A separation is made from gallium.³³ Thorium oxalate has a tendency to carry down small amounts of the sulfate ion; this makes a higher ignition temperature necessary (1200°C) to convert the precipitate to the oxide. Besides quadrivalent uranium the group of elements from which no separation is made is the rare-earth group, whose oxalates are also acid-insoluble.

Thorium oxalate is dissolved by heating with sulfuric acid or by long boiling with nitric acid. It dissolves readily in solutions containing an excess of ammonium oxalate, in carbonate solutions, and in concentrated ammonium acetate solution, and it is precipitated wholly or partially from such complexes by making the solutions acid or strongly alkaline. The complex formed with ammonium oxalate is of the type $(\text{NH}_4)_4\text{Th}(\text{C}_2\text{O}_4)_4$, and when the solution is acidified the compound $(\text{NH}_4)_2\text{Th}_2(\text{C}_2\text{O}_4)_5 \cdot 7\text{H}_2\text{O}$ is thrown down.³⁴ The rare-earth oxalates are only very slightly soluble in ammonium oxalate solutions, and separations based on this fact have been proposed. However, such methods have been severely criticized because the yttrium earths are somewhat soluble in ammonium oxalate. The poorest separation is made from yttrium.^{4,35}

Procedure. The nitrate, chloride, or perchlorate solution of thorium, which is free of sulfate and phosphate, is adjusted so that its thorium content is 100 mg or less per 100 ml, and its acid normality is 1.0 or 2.0. The use of filter pulp is helpful but is not necessary. The solution is heated to boiling, and either oxalic acid crystals (dihydrate) or a saturated solution of the same is added slowly, so that at least 100 per cent excess is present for 1N acid solution, and 400 per cent excess is present for 2N acid solutions. The suspension

is boiled a few minutes, removed from the hot plate, and allowed to stand at least 1 hr, preferably 10 hr or overnight. After filtering through a medium paper, it is washed with a solution containing 25 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and 20 ml of 12N HCl per liter.

(d) Thorium Iodate. The separation of thorium from other elements by means of the iodate is most popular because of the excellence of the separations, the rapidity of filtration of the crystalline precipitate, and the ease of re-solution. The method has been in use for years.³⁶ It has been used for the determination of traces of thorium in ores.³⁷ For macro amounts the reaction is carried out in about 6N nitric acid solution. For traces, the solutions should be 0.5N to 1N nitric acid because considerable loss of thorium is entailed at higher acid concentration. An excess of iodate reduces the solubility of the thorium iodate.

Separations are not made from zirconium and titanium; these two elements constitute the only serious interferences. Cerium(IV) and uranium(IV) are also precipitated by iodate, but if the solution is pretreated with hydrogen peroxide, the former is reduced and the latter is oxidized, and their precipitation is avoided. Sulfurous acid has also been used to reduce cerium(IV). The trivalent rare-earth ions are not affected. In the presence of appreciable amounts of rare earths, repeated precipitations may be necessary. Bismuth iodate is only slightly soluble and may be carried down with the thorium if present in large quantities; this is also possible with other elements, but it is less likely. Small amounts of phosphates do not interfere. When carried out under carefully controlled conditions, the precipitate has the composition $4\text{Th}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 18\text{H}_2\text{O}$ if potassium iodate is used as the precipitant rather than iodic acid.^{5,38,39} Because of the tendency to form such double salts the precipitates may contain the alkali metals. The method has no pronounced advantage over the simple iodate method. By using the iodate and oxalate separations in conjunction, thorium may be separated from almost all other cations.

Thorium iodate may be dissolved in reducing acids, such as hydrochloric, with the aid of a little sulfur dioxide. Boiling with an aqueous solution of oxalic acid converts the iodate to oxalate, and iodine is liberated.⁴⁰ Acidified potassium iodide solutions are also effective. This reaction is important in one of the volumetric determinations of thorium.

Thorium periodate, $\text{ThHIO}_6 \cdot 5\text{H}_2\text{O}$, is precipitated from dilute nitric acid solutions.⁴¹

Procedure (Thorium Iodate).^{6,42} The solution (100 ml), which may contain sulfuric and phosphoric acids, is treated with 50 ml of nitric acid and then with 100 ml of a 15 per cent solution of potassium iodate

in HNO_3 (1 to 1). The mixture is stirred occasionally for half an hour and is then set aside to allow the precipitate to settle; the clear liquor is decanted through a filter, and the precipitate is transferred with a 1 per cent solution of potassium iodate in HNO_3 (1 to 9). After one wash with this solution the precipitate is returned to the beaker, beaten up with 50 ml of the same solution, and again rinsed onto the filter where it is washed three times with the same solution. The precipitate is then redissolved in 30 ml of hot nitric acid and reprecipitated by the addition of 4 g of potassium iodate dissolved in HNO_3 (1 to 1) to the cooled solution that has been diluted with an equal volume of water. The precipitate is collected and washed as before and then dissolved in hydrochloric acid with the aid of a little sulfur dioxide solution. The solution contains all the thorium and any zirconium and titanium that was originally present. It is boiled with a slight excess of ammonia, the washed hydroxides are dissolved in 10 ml of HCl , and the thorium is precipitated free from other metals by the oxalate method.

Procedure (Potassium Thorium Iodate). The conditions for this precipitation are critical, and the reagents should be measured exactly. The precipitating solution is prepared by dissolving 100 g of potassium iodate in 3 per cent HNO_3 and by diluting to 1 liter with this acid. The thorium solution, which is free of cerium(IV) and contains 1 to 25 mg of thorium in 5 to 50 ml of water, is made 3 per cent in HNO_3 and mixed with an equal volume of the KIO_3 reagent. After being stirred and allowed to stand 30 min, the precipitate is filtered using a sintered-glass crucible, washed three or four times with the KIO_3 reagent diluted with an equal volume of water, then washed with several small portions of 95 per cent ethanol, and finally washed twice with ether. After the precipitate is dried at 40 to 45°C, it has the composition $4\text{Th}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 18\text{H}_2\text{O}$.

(e) Thorium Phosphates. Although thorium orthophosphate is soluble in acid and of no particular analytical importance, the pyrophosphates and hypophosphates are acid-insoluble. The pyrophosphate forms a granular precipitate that is readily filtered, but the hypophosphate forms a precipitate that is difficult to filter and runs through the paper.⁴³ Separations are made from nearly all elements except the quadrivalent cations, titanium, zirconium, hafnium, cerium(IV), and uranium(IV). Cerium(IV) is readily reduced, however, by sulfur dioxide. Separations from the rare earths are possible, but multiple precipitations may be necessary. These methods have been used in the assaying of monazite for thorium.^{29,44}

In order to precipitate thorium completely as the pyrophosphate, the solution must be boiled after the pyrophosphate⁴ is added. The acidity should be approximately 0.3N. If the acidity is too low some

thorium may fail to precipitate by forming the double pyrophosphate, $\text{Na}_4\text{Th}(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$. The addition of a strong acid to a solution containing the soluble double pyrophosphate breaks it up and causes the precipitation of thorium pyrophosphate. The pyrophosphates of cerium(III) and the rare earths do not precipitate at the acidity used. Zirconium and some titanium are precipitated from a solution under the same conditions as thorium but are later kept in solution by oxalic acid; from this solution thorium is precipitated, ignited, and weighed.

Thorium pyrophosphate is dissolved by an excess of the precipitant in weakly acid solution.⁴⁴ Also, it is not quite so insoluble in strong acids as the hypophosphate, and this behavior necessitates moderate control of the acidity of precipitation. The pyrophosphate precipitates as $\text{ThP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. It is soluble in ammonium carbonate or oxalate and on boiling with sodium hydroxide is decomposed into thorium hydroxide. Most of the phosphate may be removed by reprecipitation with sodium hydroxide. The best means found for redissolving the pyrophosphate was²⁹ to boil the precipitate with 10 to 15 per cent sodium hydroxide solution, followed by solution in nitric acid. This step is sometimes necessary when a double precipitation is made, e.g., when a separation is being made from a large amount of rare earths.

Thorium hypophosphate precipitates as $\text{ThP}_2\text{O}_6 \cdot 11\text{H}_2\text{O}$ and is quantitative even from a 10 per cent hydrochloric acid solution.^{43,45} Zirconium and titanium are also precipitated. When strongly ignited in air, the hypophosphate is partially converted to the pyrophosphate. The precipitation is complete only on heating and is then hard to filter because it runs through the filter paper. The method is not applicable as a quantitative procedure. The hypophosphate is best redissolved by oxidizing to the orthophosphate; this is accomplished by fuming with sulfuric acid, with the gradual addition of sodium nitrate. This solution is then diluted, the thorium is precipitated with ammonium hydroxide, washed, and redissolved, and the oxalate is precipitated as above.

Procedure (Thorium Pyrophosphate).⁴ Fifty milliliters of the solution, containing 0.1 to 0.2 g of thorium, is transferred to an 800-ml beaker and made up to a volume of 450 ml with distilled water. The acidity of the solution should now be 0.2N to 0.35N in H_2SO_4 . The solution is heated to boiling, stirring continuously to prevent bumping. Five milliliters of sulfurous acid is added to reduce the iron and cerium. (If the solution remains yellow, 3 or 4 drops of 10 per cent sodium thiosulfate solution will complete the reduction.) Fifteen milliliters of sodium pyrophosphate solution (50 g of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ dissolved in 1 liter of H_2O) is added from a pipet. The solution is boiled 5 min and is immediately filtered. A very convenient method of fil-

tering is to moisten a 12½-cm quantitative filter paper and press it into a Hirsch funnel that has a filter plate 8 cm in diameter, in such a way as to hold all the precipitate in the hollow thus formed.

(f) Thorium Fluoride. Hydrofluoric acid precipitates the somewhat gelatinous and highly insoluble fluoride $\text{ThF}_4 \cdot 8\text{H}_2\text{O}$ from thorium solutions. Although not suitable for quantitative work, this method does make possible certain separations and thus is of some importance. The reaction is carried out in acid solution. Centrifuging rather than filtering is necessary. Small amounts may be readily filtered when collected with mercurous chloride.³⁷

Thorium is separated from zirconium.⁴⁶ Excess fluoride complexes the zirconium and forms the soluble fluozirconate ion, but thorium is precipitated. Hafnium behaves similarly. This serves to separate thorium from those elements forming soluble fluorides or complexes with fluorides. These elements include columbium, tantalum, and tungsten. The fluoride separation proved useful in the analysis of thorium amalgams when small quantities of thorium were to be separated from gross amounts of mercury,⁴⁷ and in the determination of traces of thorium in ores.³⁷

Ions that interfere by precipitating insoluble fluorides are: uranium(IV), cerium(IV), the rare earths, and the alkaline earths. Potassium fluotitanate and fluozirconate are not very soluble and may precipitate if excessive amounts of the alkali metal are present.

When precipitated from aqueous solution, thorium fluoride is hydrated and is not nearly so resistant to re-solution as the anhydrous product. It dissolves in fluoride-complexing reagents such as boric acid and in some thorium-complexing agents such as ammonium oxalate (but not ammonium acetate). Thorium oxalate may be precipitated from the solution obtained by dissolving thorium fluoride in boric acid. The fluoride is dissolved slowly by fuming with perchloric acid. It may be converted to the oxide by pyrohydrolysis (see Chap. 29 on "Other Methods").

Procedure (5- to 50-mg Range). Ten milligrams of thorium is ideal for the precipitation of the fluoride; certainly not more than 50 mg should be present. The mildly acid solution in a celluloid centrifuge tube is treated with aqueous hydrofluoric acid (48 per cent) in excess. After stirring with a platinum rod and centrifuging, the supernatant liquid is tested for completeness of precipitation with a little more hydrofluoric acid. The precipitate is washed several times with a solution containing 1 part nitric acid and 15 parts water.

Procedure (for Trace Amounts Using HgCl as Carrier).³⁷ The solution containing the thorium is treated with 10 ml of HF and evaporated to about 8 ml. The solution is diluted with 30 ml of water and

warmed on the steam bath. To the solution is added 10 ml of mercurous nitrate solution (0.95 g of $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ in 100 ml of H_2O with 3 drops of HNO_3) and then 1 ml of dilute HCl (7 to 100). It is stirred with a platinum rod, warmed on the steam bath for a few minutes, and then allowed to stand at room temperature for about 4 hr. The solution is filtered on a Whatman No. 40 9-cm filter paper in a hard-rubber funnel and washed twice with 10 to 15 ml of approximately 5 per cent HF wash solution, the wash solution being made directly in the dish that contained the precipitate and the inside of the dish being scrubbed thoroughly with a rubber policeman wet with the solution. The precipitate is washed twice with water. The paper and precipitate are transferred to a 20-ml platinum crucible, shielded from drafts, and burned gently below 500°C in a well-ventilated hood until the paper is burned off and the HgCl is volatilized. The precipitate must be burned carefully and slowly; if the mercurous chloride is volatilized too fast, thorium may be lost by dusting. Burning at too high a temperature may convert some of the thorium fluoride to ThO_2 , which is harder to dissolve. The fluoride residue is carefully moistened with a few drops of water, and approximately 8 ml of HF is added. The crucible is covered and warmed on the steam bath for 20 min. The contents of the crucible are transferred to a platinum dish, the inside of the crucible is wet and then scrubbed thoroughly with a rubber policeman, and the vessel is rinsed into the dish. Water is added to bring the volume to 40 ml. The precipitation with mercurous nitrate and HCl is repeated as before.

(g) **Thorium Molybdate.** Ammonium molybdate precipitates thorium molybdate, $\text{Th}(\text{MoO}_4)_2$, from dilute acetic acid solutions.⁴⁸ An indicator, diphenylcarbazide, is used to determine when an excess of precipitant is present. The precipitate is gelatinous and is best filtered using filter pulp. It is readily dissolved with strong acids. The precipitation of thorium molybdate is the first step in a volumetric method of determining thorium.

Moderate amounts of calcium cause no interference, but when excessive amounts are present, some calcium is precipitated.^{49,50} Uranyl molybdate is difficultly soluble in dilute acetic acid, but its precipitation is delayed for several hours if ammonium acetate is present. Partial separations are made from the rare earths. Interferences have not been studied.

Procedure (Uranium Absent).⁴⁹ The larger part of any mineral acids present is fumed away from a sample containing 100 to 200 mg of thorium; after dilution to 150 ml the pH is adjusted to 1 to 2 with ammonia. The solution is made 7 per cent in acetic acid by adding 11 to 12 ml of glacial acetic acid. About 15 ml of thick filter pulp and

1 ml of the indicator solution (0.5 g of diphenylcarbazide per 200 ml of 95 per cent ethanol) are added. The indicator solution must be allowed to stand about two weeks before it can be used; otherwise, little or no color is developed with molybdates. A solution of ammonium paramolybdate [7.6 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ per liter] is added from a buret until the solution acquires a deep pink, and, after settling, the supernatant liquid is tested for completeness of precipitation. It is heated to boiling, filtered through a Whatman No. 42 filter paper or equivalent, and washed several times with hot acetic acid (1 to 100). When the precipitation is made for the volumetric analysis, the reaction beakers need not be scrubbed out with a policeman, because the precipitate is redissolved in these vessels.

Procedure (Uranium Present). After the addition of the glacial acetic acid in the above procedure, 5 g of ammonium acetate is added, and then the procedure is continued as before. The indicator cannot be used in the presence of ammonium acetate. The supernatant liquid is tested for completeness of precipitation.

(h) Thorium Oxinate. Thorium is quantitatively precipitated by 8-hydroxyquinoline from a buffered acetate medium.⁵¹ In the cold the precipitate is a light yellow, but on heating it becomes orange-red. Like the corresponding uranyl derivative, thorium 8-hydroxyquinolate forms an addition compound with an extra mole of the reagent, forming $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$.⁵² The pH of the precipitation is important; no reaction occurs at a pH lower than 3.7 or higher than 12.5, and the lowest pH for quantitative precipitation is 4.4.^{53,54} The precipitate may be weighed or titrated for the determination of thorium.

Numerous other metals are, of course, precipitated by oxine, and thus the possible separations are few. Cerium(III) is not precipitated, however; this property affords a means of separating it. Subsequent treatment with a tartrate and ammonia does precipitate the cerium⁵⁵ (for procedure, see Sec. 4.2d).

(i) Thorium Cupferrate. Thorium is carried down by cupferron to some extent when other cupferron-precipitable elements are present, even from very strong sulfuric acid solutions,⁵⁶ but quantitative precipitation is not possible below a pH of about 4. Traces of thorium in 10 per cent H_2SO_4 solution are not removed when a chloroform extraction of the cupferrates is made. In acetic acid solution thorium is precipitated quantitatively, but free sulfuric acid must be absent.⁵⁷

It has been found that thorium is precipitated from its carbonate complex by cupferron⁵⁸ at a pH of 4 with a recovery of about 98 per cent from known mixtures. Thorium cupferrate may be extracted with chloroform from such a mixture. Uranium(VI) will not precipitate or be extracted by chloroform under these conditions.

Procedure.⁵⁸ Approximately 100 ml of a sulfuric acid solution containing 100 to 200 mg of thorium is cooled until the temperature is below 15°C. To the solution is added a calculated amount of ammonium carbonate solution (20 per cent) sufficient to partially neutralize the acid, complex any uranium present, and bring the pH to 3.5 to 4.5. After cooling to 5°C, 25 ml of cupferron solution (6 per cent) is added, and the mixture is stirred for 5 min. The precipitate is filtered on a Whatman No. 42 filter paper, using a filter cone and gentle suction, and it is washed well with cold water.

(j) Precipitation with Benzenearsonic Acid and Its Derivatives. Benzenearsonic acid (phenylarsonic acid) precipitates titanium, zirconium, hafnium, and thorium as well as a few other elements, such as tin(IV), columbium, and tantalum. The titanium, zirconium, and hafnium may be precipitated from strongly acid solutions, but thorium requires a buffered acetate medium.⁵⁹ The precipitate is very easily filtered and washed.

The rare earths are coprecipitated to some extent with thorium benzenearsonate, and a double precipitation is usually necessary.⁵⁹ Cerium(IV) and uranium(IV) are also precipitated.

Several derivatives of benzenearsonic acid have been employed with the metals mentioned above other than thorium.⁶⁰ For microgram amounts *p*-dimethylaminoazobenzenearsonic acid ('pararsonic acid') has been satisfactory.^{37,61} This is employed in a colorimetric method for determining thorium.³⁷ In one procedure, the precipitation is carried out in solutions of pH 1 to 2. It has been stated that zirconium may be separated by a prior treatment with the reagent⁶¹ in a highly acid solution. Uranium(VI) and calcium do not interfere.

Procedure (with Benzenearsonic Acid). A nitrate or chloride solution of thorium containing about 100 mg of thorium in 100 to 200 ml of water is adjusted to a pH of 1 to 3, and 30 ml of a 10 per cent benzenearsonic acid is added, followed by 75 ml of glacial acetic acid. Prior to this treatment any cerium(IV) present is reduced with sulfurous acid. A 50 per cent solution of ammonium acetate is added until further addition causes no further precipitation, and the mixture is digested for 10 min at 80 to 90°C. The precipitate is filtered off and washed with water that contains a little acetic acid and ammonium acetate. The precipitate is dissolved in 6N hydrochloric acid for a second precipitation in case any considerable amount of the rare earths is present; a few more milliliters of the reagent solution should be added before buffering the second time with ammonium acetate.

Procedure (with *p*-Dimethylaminoazobenzenearsonic Acid in Microgram Amounts).⁶¹ The *p*-dimethylaminoazobenzenearsonic reagent

is prepared by dissolving 0.1 g in a mixture of 95 ml of ethanol and 5 ml of HCl, stirring, allowing to settle overnight, and filtering through a fine sintered-glass crucible. The thorium solution (generally 3 to 4 ml, containing up to 10 γ of thorium) is adjusted to a pH of 1 to 2 and diluted to 5 ml, and 1 ml of the pararsonic acid reagent is added. After the solution has stood at least 15 min, the small amount of precipitate is filtered off on a glass-fritted crucible, a porcelain disk, or an asbestos mat and is washed with 4 ml of a mixture made from 1 ml of HCl and 99 ml of ethanol.

Procedure (with *p*-Dimethylaminoazobenzearsonic Acid).³⁷ A solution of the thorium, in 43 ml of water containing 4 drops of HCl, is neutralized with ammonia using 2 drops of methyl red as indicator. A solution of HCl (7 to 100) is added drop by drop until the methyl red just turns red, and then 1.2 ml is added in excess. Five milliliters of a solution of *p*-dimethylaminoazophenylarsonic acid, 0.1 g in 50 ml of alcohol solution (1 to 1) containing 10 g of $\text{CH}_3\text{COONH}_4$ is now added. The beaker is covered, and the mixture is allowed to digest on the steam bath until the precipitate clots (10 to 20 min). The precipitate is filtered on a 10-ml Gooch filter covered with asbestos and washed four times with 10-ml portions of the ammonium acetate wash solution, which contains 10 g of $\text{CH}_3\text{COONH}_4$ and 12 ml of HCl (7 to 100) in 488 ml of H_2O .

(k) Precipitation with *m*-Nitrobenzoic Acid. The precipitation of thorium with *m*-nitrobenzoic acid has been used for years.^{4,62,63} All three nitrobenzoic acids precipitate thorium, but the meta acid is more readily prepared and is more soluble than its ortho and para isomers. The thorium is precipitated from solutions free from excess mineral acid. It has the composition $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{COO})_4$. It is easily filtered and settles readily. It is decomposed by both mineral acids and bases. Tartrates prevent its precipitation.

Double precipitation accomplishes a fair separation of thorium from lanthanum, cerium, and most of the other rare earths. Zirconium does not precipitate unless present in excessive amounts, and this is true of most other cations. Iron(III) and uranium(VI) form colored compounds with the reagent but do not precipitate.

m-Nitrobenzoic acid is used for precipitating milligram amounts of thorium even in the presence of large quantities of uranium. It may be decomposed, and the *m*-nitrobenzoic acid that is formed may be reduced to the amino compound and coupled with β -naphthol to form a dye in the colorimetric determination of thorium.

Procedure.⁴ The reagent is prepared by dissolving 4 g of *m*-nitrobenzoic acid in 1 liter of hot water, allowing the solution to stand overnight, and filtering before use. Any excess mineral acid is neutralized with ammonium hydroxide until a permanent precipitate of

thorium hydroxide is formed. The precipitate is then redissolved in the minimum amount of dilute nitric acid. For each 100 mg of thorium present in the neutral solution, 150 ml of the reagent is added with stirring. After the solution is heated to 60 to 80°C for at least 15 min, the precipitate is filtered off and washed with either water or the precipitating solution that has been diluted 1 to 4.

The precipitate is next dissolved into the precipitation beaker by hot HNO_3 (1 to 5), the paper is washed well with hot water, and the solution is diluted to 600 ml. Methyl orange is added to a decided red color, followed by 25 ml of *m*-nitrobenzoic acid. The solution is neutralized with ammonium hydroxide (1 to 10) until a pink color, due to the weak organic acid, is reached. As the excess of HNO_3 is neutralized, the thorium precipitates again as *m*-nitrobenzoate. If the process of neutralization is carried too far, that is, to the yellow tint, rare earths that may be present are likely to precipitate. After the pink color is reached, 50 ml more of the precipitant is added to ensure complete precipitation. The solution is then heated as before, filtered, and washed.

(l) Precipitation with Picrolonic Acid. Picrolonic acid precipitates thorium from acetic acid solutions as a voluminous product and is particularly suited for milligram quantities of thorium.⁶⁴ The pH must be controlled between the limits of 2.0 and 3.2 for complete precipitation.⁶⁵ A potentiometric method for the determination of thorium is based on titration of the precipitate.

Few separations of thorium from other elements are made by the use of picrolonic acid. The rare earths and most heavy metals are carried down.

Procedure. The precipitating solution is prepared by dissolving 2.6 g of picrolonic acid in 1 liter of water. Any mineral acid present in the thorium solution, which should be 50 to 60 ml in volume and should contain not more than 10 mg of thorium, is just neutralized with dilute sodium hydroxide. Any precipitate formed is redissolved by adding glacial acetic acid and heating if necessary. Enough acetic acid is added until the solution is 2.5 per cent in acetic acid. The solution should be free of ammonium salts. Fifty milliliters of the picrolonic acid solution is added; the solution is stirred, allowed to stand 15 min or more, and filtered; and the precipitate is washed with water.

(m) Precipitation with Ferron. Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) has been used to precipitate thorium from solutions at pH 2.0 to 3.5.⁶⁶ The yellow precipitate is easily filtered.

The compound that is formed contains two ferron molecules per thorium atom. Sulfates interfere in the precipitation. Good separations from uranium(VI) are made if the uranyl salt is not present in

excessive amounts. The method was developed for use in the presence of uranium alone and is not applicable when other elements are present.

Procedure.⁶⁶ A few drops of bromophenol blue are added to the mildly acid solution containing thorium; the solution is then buffered with ammonium acetate until the color is blue. Dilute hydrochloric acid is added until the color becomes yellow (pH about 3). After the solution has been heated to 60 to 80°C, 0.2 per cent ferron solution is added with stirring; 4 ml of reagent is used for each milligram of thorium, but not less than 40 ml is used in any case. The light-yellow precipitate is digested for half an hour, filtered on a Whatman No. 42 filter paper or its equivalent, and washed with a 0.02 per cent ferron solution.

(n) Precipitation with Sebacic Acid. Thorium sebacate is quantitatively precipitated from mildly acid solutions.⁶⁷ The precipitate is flocculent and readily filtered. The method is inaccurate in the presence of large excess of cerium and requires preliminary separation.^{68,69} Separations are made from most of the cerium and yttrium earths unless these are present in excessive amounts. The method has not been used extensively.

Procedure.⁶⁷ The thorium solution is treated with ammonia until a permanent precipitate is formed, and this is just redissolved by adding nitric acid. A slight excess of sebacic acid dissolved in hot water is added to the boiling thorium solution. After the mixture has digested at 90 to 100°C for about 15 min, the precipitate is filtered off and washed with hot water.

(o) Precipitation with Miscellaneous Reagents. It is well known that thorium forms a double sulfate with potassium which is difficultly soluble and which may serve in some separations of thorium. Thorium is also coprecipitated to some degree when barium sulfate is thrown down from an acid solution.⁷⁰ Thorium ferrocyanide and thorium arsenates are precipitated from moderately strong acid solutions. They are of little value for analytical determinations.

Numerous organic acids precipitate thorium. Among them are mucic, anisic, aspartic, salicylic, tannic, and phenoxyacetic acids (see references 4, 62, 67, and 71).

Metzger⁷² found that from a 40 per cent alcoholic solution thorium is precipitated quantitatively as thorium fumarate on the addition of fumaric acid. According to Giles⁷³ a suspension of lead carbonate precipitates thorium, zirconium, cerium(IV), and iron(III) completely. Barium carbonate and zinc oxide have been used also. The zinc oxide method is less affected by rare earths than the other.⁷⁴

1-(*o*-Arsenophenylazo)-2-naphthol-3,6-disulfonic acid forms a red precipitate with thorium salts; moderate amounts of zirconium and the rare earths do not interfere.⁷⁵

Thorium salicylate is precipitated from buffered acetate solutions; zirconium is also precipitated but not titanium.⁷⁶

Sodium acetylacetonate when added to thorium solutions precipitates thorium acetylacetonate. Benzenesulfinic acid ($C_6H_5SO_2H$) and sodium alizarin-3-sulfonate give precipitates with thorium solutions.⁵

(p) Precipitation with Carriers. Carriers have not been used to such a great extent for the determination of traces of thorium as with uranium. The greatest use of carriers has been that of mercurous chloride,³⁷ whereby thorium fluoride is carried by means of mercurous chloride.

This procedure is given under (f) of this section. Some preliminary experiments⁷⁷ indicate that complete precipitation and recovery of microgram quantities of thorium can be obtained by using aluminum as carrier.

3.2 Volatilization. Volatilization methods of removing thorium from other elements for analytical purposes are not convenient and are rarely employed. Some separations have been made by fractional distillation under vacuum of thorium acetylacetonate.^{78,79} The acetylacetonate is precipitated from aqueous solution, dried, and distilled. The distillate is decomposed with nitric acid. Many other elements also form acetylacetonates, and careful fractionations are required to achieve a given separation.

Thorium chloride may be separated by sublimation from nonvolatile chlorides. This is accomplished by passing a mixture of chlorine and sulfur monochloride vapor (S_2Cl_2) over thorium dioxide or certain other compounds at 700 to 780°C.^{80,81} Separations are said to be made from the rare earths.

3.3 Complex Formation. Many of the precipitates discussed above are Werner complexes of thorium. Besides these, complexes include water-soluble substances, extractable substances, and some volatile compounds; there is accordingly no sharp distinction between these various groups.

Thorium salts form complexes with ketones,^{82,83} aldehydes,⁸²⁻⁸⁴ and amines.⁸⁵ Examples are complexes with acetone, $ThCl_4 \cdot 2(CH_3)_2CO$; with salicylaldehyde, $ThCl_4 \cdot 2C_6H_4OHCHO$; with pyridine, $Th(NO_3)_4 \cdot 4C_5H_5N \cdot HNO_3$; with β -naphthylamine, $ThCl_4 \cdot C_{10}H_7NH_2$; and with antipyrine, $Th(NO_3)_4 \cdot 4C_{11}H_{12}N_2O$. Although these have no particular analytical applications, many others do, including the precipitates already mentioned. (Thorium complexes with oxine,⁵¹ cupferron, picrolonic acid,⁶⁴ ferron, acetylacetone,⁷⁸ and salicylic acid.⁷⁶)

Thorium forms several water-soluble complexes of considerable analytical importance. Carbonates precipitate basic thorium carbonate, ThOCO_3 , which redissolves in an excess of the reagent. The carbonate complex is decomposed by acids. Thorium oxalate is dissolved by ammonium, sodium, or potassium oxalate and forms a complex of the type $(\text{NH}_4)_4\text{Th}(\text{C}_2\text{O}_4)_4$. The oxalate complex is decomposed into thorium oxalate by mineral acids and into thorium hydroxide by alkalis. Thorium oxalate also dissolves in concentrated ammonium acetate solution. Thorium fluoride dissolves slowly in oxalates. Malonates form a complex with thorium similar to that with oxalates.⁸⁶

Tartrates and citrates and salts of similar hydroxy acids form complexes with thorium which are stable in alkalis. The complex formed with sulfosalicylic acid is also alkali-stable.⁸⁷ Catechol forms complexes with numerous metals, including thorium,⁸⁸ which forms still another with catechol and pyridine, $\text{Th}(\text{OC}_6\text{H}_4\text{OH})_4 \cdot 2\text{C}_5\text{H}_5\text{N}$.⁸⁹

4. METHODS OF DETERMINATION

The methods of determining thorium are predominantly gravimetric, and involve ignition to thoria and weighing. This is the method ordinarily preferred when only a few samples are to be analyzed, and it is the most accurate. Ordinarily the thorium is precipitated as the hydroxide, peroxide, or oxalate and ignited to the dioxide. The titrimetric methods are most useful when numerous samples are to be analyzed, but they usually involve considerable preliminary separation. The technique that involves the precipitation of thorium molybdate and then reduction and titration of molybdenum has been used to advantage when there are no interfering elements present. The titration of iodine from $\text{Th}(\text{IO}_3)_4$ or $\text{KIO}_3 \cdot 4\text{Th}(\text{IO}_3)_4$ has been employed to a limited extent for amounts of thorium from 5 to 50 mg.⁹⁰

The procedures for the determination of traces of thorium, up to about 1 mg, are relatively few, but of those which have been worked out, colorimetric methods using 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid and pararsonic acid have been employed to the greatest extent. The *m*-nitrobenzoate has been used by reducing it to the corresponding amino compound.

The most reliable primary standard for thorium is the dioxide that is prepared by igniting the purified nitrate to 1100 to 1200°C in a muffle and by cooling in a desiccator. Standard thorium solutions are almost always prepared from a soluble salt and then standardized gravimetrically, however, because of the difficulty with which the dioxide is dissolved.

4.1 Gravimetric. The weighing form for thorium employed in its gravimetric determination is nearly always the dioxide, ThO_2 . Two other weighing forms are the oxinate, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$, and the pyrophosphate, ThP_2O_7 , of which the latter may not have an entirely reproducible composition and cannot be recommended. When thorium in small amounts is being determined or is being separated from other elements by the use of 8-hydroxyquinoline, the oxinate affords a convenient weighing form; it contains 24.3 per cent thorium. It may also be ignited to thoria, or dissolved, and titrated.

(a) Ignition to Thoria. Thorium hydroxide, peroxide, and oxalate are usually ignited to the oxide. The nitrate, after dehydration, which is carried out carefully to prevent spattering, is easily converted to the dioxide. The sulfate requires a high temperature (1200°C), and accurate analyses are not obtained. This also applies to materials that contain appreciable amounts of sulfur, such as thorium peroxide sulfate. The benzenearsonate slowly ignites to thoria, but in practically all cases arsenic is retained. According to some authors⁵⁹ ignition of the benzenearsonate is not recommended, because it is simpler to dissolve the thorium compound and to reprecipitate the thorium as the oxalate.

Thorium iodate, $\text{Th}(\text{IO}_3)_4$, freed of $4\text{Th}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 18\text{H}_2\text{O}$ is easily ignited to the dioxide; the double potassium salt is converted by metathesis with oxalic acid, and the oxalate is filtered and ignited. Thorium peroxide, chloride, perchlorate, and nitrate all ignite to thoria, but the peroxide sulfate, as already mentioned, causes some difficulty. The following fail to ignite to thoria: thorium hypophosphate or pyrophosphate, thorium molybdate, and thorium fluoride.

Many of the organic derivatives of thorium may also be ignited to the oxide. They generally form a melt, which may froth and spatter unless precautions are taken. Furthermore, some of the compounds may volatilize to some extent, but this can be prevented by covering the precipitate with solid oxalic acid before ignition; this may not be successful in the case of thorium acetylacetonate. Compounds that may be quantitatively ignited to thoria with oxalic acid crystals include the oxinate, cupferrate, *m*-nitrobenzoate, picrolonate, sebacate, and salicylate. Apparently the ferron derivative of thorium may be ignited to thoria despite its sulfur content.⁶⁶

(b) Thorium Hydroxide, Peroxide, and Oxalate. When thorium is to be determined gravimetrically it is ordinarily precipitated as the hydroxide, peroxide, or oxalate, is filtered, and is ignited to the oxide. This method is applicable in the absence of interfering ions. Other materials, as mentioned above, may also be ignited. Thoria is not hygroscopic if ignited above 950 to 1000°C . Errors of about ± 0.1 per cent can ordinarily be expected.

Procedure. The thorium hydroxide, oxalate, or other suitable compound, when precipitated as mentioned under Sec. 3, "Methods of Separation," is filtered with suction, using ashless filter paper with a platinum filter cone or equivalent and is dried at 110°C in a weighed platinum or quartz crucible. The precipitate is cautiously heated with a flame, and the paper is burned away. After ignition to thoria with the full heat of a Meker burner, the crucible is placed in a muffle at 1000°C or above for about 15 min. After it has cooled in a desiccator, the ThO_2 is weighed.

(c) Thorium Oxinate. Thorium oxinate, when precipitated with an excess of oxine, contains an extra molecule of oxine of crystallization. This extra molecule of oxine is very slowly lost at 130 to 140°C and is completely lost in 3 hr at 160 to 170°C .⁵² The color of the material changes from an orange-red to a light yellow. Even after an extra molecule of oxine is lost, the remaining material, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4$, is not completely stable at 160 to 170°C . It is recommended that the thorium be weighed as $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$,⁶⁴ which is dried to practically constant weight at 130°C . Errors are about ± 0.2 per cent.

Procedure. The thorium oxinate precipitate is filtered using a sintered-glass crucible and is well washed with water at room temperature. It is dried at 130 to 135°C to practically constant weight (about 2 hr), cooled in a desiccator, and weighed. If it is desired to ignite to ThO_2 , the oxinate is filtered on paper which is placed in a platinum crucible and covered with solid oxalic acid. It is then cautiously ignited as with the hydroxide.

4.2 Volumetric. Because of the constancy of the valence of the thorium ion, titrimetric methods are not well adapted to its determination. As a result the available volumetric methods are somewhat slow, are not especially accurate, and involve the precipitation of an insoluble thorium compound. The excess of the precipitating agent is determined with an indicator or electrometrically, or, in most cases, the insoluble thorium compound is filtered and washed, and the thorium is determined indirectly by some reaction of the acid radical of the salt (molybdate, iodate, oxalate, oxinate, etc.).

(a) Molybdate Method. The thorium solution, made weakly acidic with acetic acid, is titrated with a standard ammonium molybdate solution, and diphenylcarbazide is used as an outside indicator.⁴⁸ The difficulty of the method is that a fair excess of molybdate is required to give the pink color, which forms slowly; thus a relatively large blank is introduced. Any appreciable amount of uranium interferes, but moderate amounts of calcium and the rare earths can be tolerated. The method is rapid, but errors are as high as 2 per cent.

The excess of molybdate may also be detected electrometrically.⁴⁹ The titration is carried out as before, using a 0.1N calomel reference electrode and a molybdenum-wire indicator electrode. Even very large amounts of calcium do not interfere. Errors are ± 0.3 per cent. A third variation of the molybdate method consists in precipitating thorium molybdate, filtering, washing, redissolving, and determining the molybdenum in the usual manner.⁴⁹ This determination is made by reducing the molybdenum to the trivalent state in an amalgamated zinc-filled Jones reductor, catching the reduced solution in ferric alum, and titrating the ferrous iron formed with ceric sulfate. No interference is encountered from those elements which are not carried down by thorium molybdate; these include moderate amounts of calcium, the rare earths, and uranium, although modified precipitation conditions are necessary in the presence of the last element (see Sec. 3.1g). Other interferences have not been studied. The method is somewhat time-consuming but not prohibitively so. Errors are of the order of 0.5 per cent.

Procedure (Direct Titration).^{48,49} A volume of thorium solution that contains 100 to 200 mg of thorium is taken and diluted to 150 ml, and the pH is adjusted to 1 to 2 with ammonia. Any large quantity of hydrochloric or nitric acid is fumed off before adjusting the pH. Eleven to twelve milliliters of glacial acetic acid is added, and the solution is titrated with constant stirring with a standard ammonium molybdate solution, until a drop gives a faint pink color when added to a little indicator solution in a white spot plate. The indicator is prepared by dissolving 0.25 g of diphenylcarbazide in 100 ml of 95 per cent ethanol and allowing it to stand at least two weeks before use. The ammonium molybdate solution is prepared by dissolving 7.6 g of the salt, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 1 liter of water; this is standardized by titration of a known volume of standard thorium nitrate solution that contains 11 ml of glacial acetic acid per 150 ml. A blank should be run. Some experience is required for good results.

Procedure (Electrometric Titration).⁴⁹ The solutions are prepared for titration as in the direct-titration method above. The beaker in which the titration is to be carried out is equipped with a 0.1N calomel reference electrode and a molybdenum indicator electrode and is connected to a potentiometer. The temperature is raised to 50 to 55°C and maintained until the titration is finished. The volume of ammonium molybdate that is used is plotted against the potentiometric readings, and the end point is determined from the curve.

Procedure (Titration of Molybdenum in Molybdate).⁴⁹ Samples containing 0.15 to 0.2 g of ThO_2 are weighed and placed in 250-ml

beakers. After the samples have been dissolved, any large excess of mineral acid is destroyed by evaporating the solutions nearly to dryness. The samples are then diluted to 150 ml with water and made about 7 per cent in acetic acid by adding 11 ml of glacial acetic acid. Fifteen milliliters of thick filter pulp and 1 ml of a diphenylcarbazide solution (0.5 g per 200 ml of 95 per cent ethanol) are added. The ammonium paramolybdate solution (7.6 g per liter) is added from a buret with stirring until the indicator imparts a deep pink color to the solution. After the precipitates have settled, the supernatant liquid may be tested for complete precipitation. The contents of the beakers are heated to boiling and filtered while hot through Whatman No. 42 11-cm filter papers into 400-ml beakers. The precipitates are washed five or six times with hot acetic acid (1 to 100). The 250-ml beakers need not be scrubbed with a policeman, but they should be carefully rinsed out two or three times with wash solution. The washed precipitates and filters are transferred to the 250-ml beakers that were used to carry out the precipitations, and 25 ml of HCl is added to each beaker. The contents are stirred until the filters disintegrate. Seventy-five milliliters of water is added, and the mixture is heated to boiling and filtered while hot through a Whatman No. 42 11-cm filter paper into a 400-ml beaker. (Long boiling results in reduction of molybdenum and decomposition of the filter pulp.) The filter pulp and filter are washed five or six times with hot HCl (1 to 100). After the filtrates have cooled to room temperature, they are passed through a Jones reductor into an excess (five times the theoretical) of 10 per cent ferric alum, to which 2 to 3 ml of H_3PO_4 has been added, and titrated with 0.1N ceric sulfate. Two drops of ferroin are used as indicator. The end point is taken as that point at which the pink color of the solution changes to colorless or light blue.

(b) Iodate Method. This procedure consists of precipitating thorium iodate⁹⁰ or potassium thorium iodate,³⁸ washing, and redissolving in acidified potassium iodide. The iodine that is liberated is titrated with sodium thiosulfate. The method is moderately rapid and is especially adapted to the determination of less than 10 mg of thorium. Errors for this method are about 1 per cent.

Procedure.^{9,90} Five milliliters of the test solution, which contains 1 to 10 mg of thorium, is placed in a graduated 15-ml centrifuge cone, and 2.5 ml of HNO_3 is added, followed by 5 ml of the iodate reagent (15 per cent KIO_3 in 50 per cent HNO_3). After it has been mixed, the suspension is centrifuged at about 2,000 rpm. Thorium iodate, which is difficult to filter, gives, under these conditions, a compact, easily separated precipitate. The supernatant liquid is poured off, and the precipitate is mashed up with 8 ml of water and recentrifuged. This

washing is carried out four times; it was found that this is sufficient to remove all significant amounts of soluble oxidizing agents. Approximately 2 g of potassium iodide is then added to the tube in the form of a strong aqueous solution; then sufficient HCl is added to dissolve the precipitate. The resulting iodine solution is rinsed into a conical flask and titrated with 0.1N sodium thiosulfate; no indicator is employed.

(c) Oxalate Method. The composition of thorium oxalate apparently varies with the mode of precipitation. When formed by the addition of oxalic acid or an oxalate to the thorium solution, the precipitate may be as much as 3 per cent deficient in oxalate, but by reversal, that is, by adding the thorium solution to the oxalic acid, the theoretical composition is attained.⁹¹ This affords a volumetric method for the determination of thorium, and although it is inconvenient to add the thorium solution to the oxalic acid, the errors are said to be small.

Procedure.⁹¹ An excess of oxalic acid is heated, and the hot thorium solution is added gradually with stirring. It is important to add the thorium to the oxalic acid rather than vice versa. After the mixture has digested for 15 to 30 min on the steam bath, the precipitate is filtered off on a Gooch crucible with an asbestos mat or a fritted glass filtering crucible and washed well with cold water that contains 4 drops of H_2SO_4 per 100 ml. The crucible with precipitate is placed in a beaker that contains 100 ml of water and is heated to about 85°C , and 5 ml of H_2SO_4 (1 to 1) is added. Standard potassium permanganate is added until the larger part of the precipitate is dissolved; the temperature is again raised to 85°C , and the titration is completed. The end point is sharp if the solution is kept hot. A preferable titration method consists of adding an excess of ceric sulfate to the thorium oxalate from a buret or pipet, heating until the oxalate is all oxidized, cooling, and titrating the excess ceric ion with ferrous sulfate, ferroin being used as indicator.

An alternative technique is to use a known volume of standard oxalic acid as the precipitating agent. After filtering, the excess oxalic acid in the filtrate is titrated.

(d) Oxinate Method. Thorium oxinate, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$, is precipitated, washed, and redissolved in acid. The 8-hydroxyquinoline thus formed is titrated with potassium bromate,⁹² and 5,7-dibromo-8-hydroxyquinoline is formed. Errors are about 1 per cent.⁵¹

Procedure.⁵¹ The solution containing 10 to 100 mg of thorium in 50 to 200 ml of water is treated with 5 ml of 2N acetic acid if no excess mineral acid is present and is heated to about 90°C . In the presence of mineral acid, ammonium hydroxide is added just to the point of precipitation. The slight precipitate that is formed is then

dissolved in acetic acid, and the solution is treated as above. An excess of 8-hydroxyquinoline (2.5 g dissolved in 6 ml of glacial acetic acid and diluted to 100 ml) is added slowly, and the solution is brought to a boil. Ammonium acetate (2N) is slowly added until a permanent precipitate forms, and then 20 to 25 ml more is added. The mixture is allowed to cool to room temperature, and the precipitate is filtered off on a sintered-glass crucible and washed with cold water. The precipitate is dissolved from the filter with 2N HCl, and the filter is washed well. The filtrate and washings are caught in an iodine flask, and 1 g of potassium bromide and 2 to 4 drops of 0.1 per cent methyl red (sodium salt) are added. The solution, which is stirred continuously, is titrated slowly with standard potassium bromate (0.1N) until the color changes from red to yellow. Two or three more milliliters of bromate is added, and the mixture is allowed to stand a few moments in the stoppered flask. A gram of potassium iodide is added, and the iodine that is liberated is titrated with sodium thiosulfate. Instead of titrating with KBrO_3 , an amount that is known to be an excess may be pipetted in and the excess back-titrated as above.

(e) Miscellaneous Titrimetric Methods. Various electrometric titration methods for thorium have been investigated, all of which are lengthy, and none of which at the time of writing were superior to the methods discussed above. These include electrometric titration with sodium or ammonium oxalate, a method in which the rare earths interfere but which is otherwise successful;⁹³ potentiometric titration of thorium picrolonate in a CO_2 atmosphere with a titanous salt, which reduces a nitro group to an amino group;⁹⁴ and potentiometric titration with potassium ferrocyanide using a 30 per cent alcoholic solution.⁹⁵

4.3 Colorimetric. The colorimetric methods for the determination of thorium are relatively few. Because the ion is colorless, the methods depend upon the formation of a colored derivative or a compound from which a color may be developed.

(a) Pararsonic Acid. The highly insoluble and highly colored thorium derivative of *p*-dimethylaminoazophenylarsonic acid ("pararsonic acid") may be precipitated, filtered or centrifuged, washed, and treated with ammonia or sodium hydroxide.³⁷ The color of the solution that is formed may be measured with a spectrophotometer.⁶¹ The method is applicable for amounts of thorium in the range of 0.5 to 500 γ , and by proper choice of size of sample and cuvette the limits may be varied widely. Zirconium interferes because its salt of pararsonic acid is even more insoluble than the thorium salt; however, it has been stated that it is possible to remove zirconium in reasonably small amounts by precipitating it in very strongly acid solution (pH -1 or 0) with the reagent.⁶¹ Excessive amounts of uranium inter-

fere, but when the uranium/thorium ratio is not over 1,000 the interference is negligible. Errors are about 10 per cent and can be lowered by careful standardization of technique. The following procedure has been used for the determination of thorium in ores and minerals. The spectral transmittancy of the dye solution that is obtained is shown in Fig. 2.1.

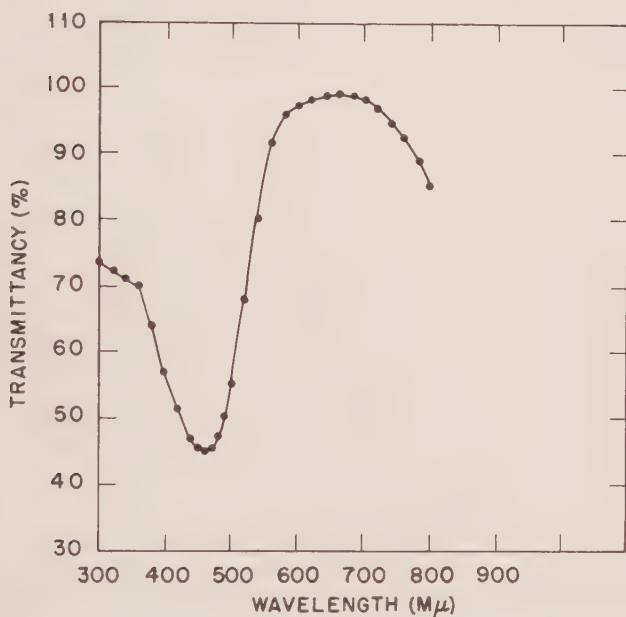


Fig. 2.1—Spectral transmittancy curve for the photometric determination of thorium with *p*-dimethylaminoazophenylarsonic acid. Data were obtained with the Coleman universal spectrophotometer model 11, using water as reference. The concentration used was 0.1 mg of ThO_2 per 100 ml.

Procedure.³⁷ After the thorium compound has been precipitated, filtered, and washed as described in Sec. 3.1j, it is dissolved from the filter crucible with 30 ml of a warm 4 per cent solution of NaOH. The crucible is washed once with water, the combined solutions are diluted to 250 ml, and the per cent transmittancy is measured at 460 $\text{m}\mu$ on a spectrophotometer. The percentage of thorium is obtained from a transmittancy-concentration curve made from known amounts of thorium that were carried through the above procedure.

(b) 1-(*o*-Arsenophenylazo)-2-Naphthol-3,6-Disulfonic Acid. This compound forms a strawberry-red precipitate with thorium salts,⁷⁵

and this serves as the basis of a colorimetric determination. It can be used without separation from the excess reagent,⁹⁶ but the absorption bands are such (Fig. 2.2) that the amount of reagent must be carefully measured, and an idea of the approximate thorium range

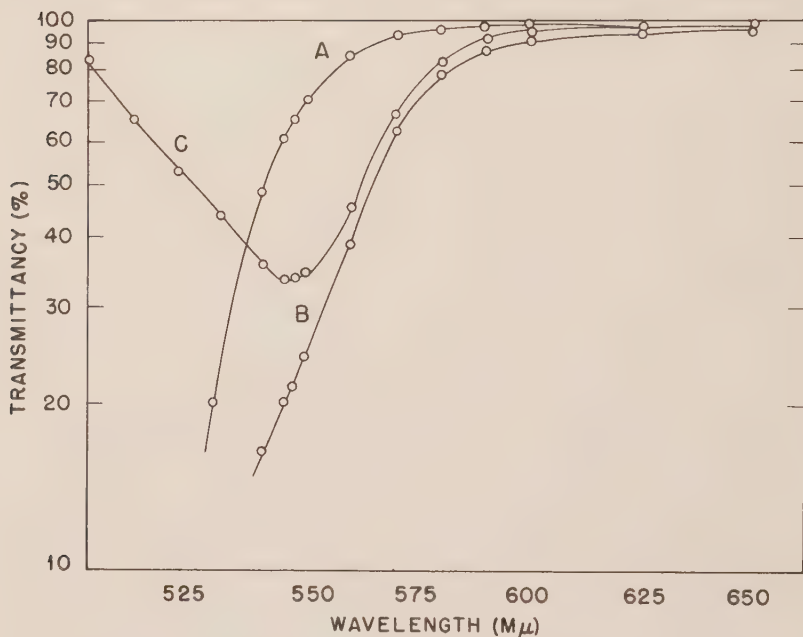


Fig. 2.2—Spectral transmittancy curves of (1-o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. Curve A: Reagent against water. Curve B: Reagent plus thorium against water. Curve C: Reagent plus thorium against reagent.

must be known. The method has been used for the determination of microgram quantities of thorium, and the color is stable for at least 24 hr. The best pH range is 0.3 to 1. Errors are about 5 per cent when a carefully standardized technique is used.

Zirconium and uranium(IV) interfere, but uranium(VI) does not interfere even when present in 1,000 times the amount of thorium. Iron does not interfere if first reduced with hydroxylamine. With less than 100 γ of thorium, 1 mg of each of the following ions causes negligible interference: lead, barium, calcium, zinc, aluminum, copper, nickel, sodium, ammonium, and ferrous. As a matter of fact 16 mg of calcium or 10 mg of ammonium does not interfere.

Procedure.⁹⁶ The sample containing 5 to 100 γ of thorium is evaporated with HNO_3 several times; the last time it is evaporated almost to dryness. The residue is taken up in 0.5 ml of HNO_3 , and 0.5 ml of HCl and 1 ml of 70 per cent HClO_4 are added, and the solution is evaporated to dryness. The residue is treated with 5 drops of HCl and rinsed into a 10-ml glass-stoppered volumetric flask. One milliliter of 0.1 per cent aqueous reagent is added, and the solution is made up to 10 ml and transferred to a cuvette. Transmittancies are measured at 545 $\text{m}\mu$ against a reference solution that consists of 5 drops of HCl and 1 ml of the reagent solution diluted to 10 ml. The composition of the reagent varies a little from batch to batch, and this causes the stock solutions to vary in color. Furthermore, some of the reagent solutions are not entirely stable and fade slightly after first being made.

Another method consists of the precipitation of thorium *m*-nitrobenzoate, reduction of the nitro group to the amino group, diazotization, and coupling with β -naphthol to form an orange dye, which can be determined colorimetrically.^{97,98} The principal faults of the method are its complexity, the lack of precision, and the relatively high solubility of thorium *m*-nitrobenzoate.

(c) **Iodine Liberation.**⁹⁹ When thorium iodate is reduced with hypophosphorous acid in the presence of H_2SO_4 , iodine is liberated. By causing the reaction to take place in the presence of carbon tetrachloride, the iodine liberated is immediately dissolved, and imparts a bluish-red color to the carbon tetrachloride. Because the iodine liberated is directly equivalent to the thorium iodate reduced, a color measurement of the carbon tetrachloride-iodine solution may be used as an indirect measurement of the thorium iodate. Because the measurement is indirect, it is essential that the thorium iodate be free of any other iodate.

Figure 2.3 shows the spectral transmittancy curve of a solution of iodine in carbon tetrachloride. There is a definite minimum transmittancy at 520 $\text{m}\mu$. Beer's law is obeyed.

Procedure.⁹⁹ The $\text{Th}(\text{IO}_3)_4$ precipitate is allowed to settle overnight. The supernatant liquid is decanted through a Whatman No. 42 4-cm filter paper, and finally the precipitate is transferred to the paper using a fine jet of 76 per cent alcohol (80 ml of 95 per cent alcohol diluted with distilled water to 100 ml). The paper is washed three times with the alcohol solution. A spectrophotometer cell is placed under the funnel, and the filter paper is treated with 1 ml of H_2SO_4 (1 to 1); this brings the acid into contact with all parts of the paper. After 5 min the paper is washed six times with distilled water.

The total washings should not exceed 10 ml. Ten milliliters of carbon tetrachloride is added to the solution in the cell, 0.2 ml of hypophosphorous acid is added, and the tube is stoppered and shaken for 2 min. The transmittancy is immediately measured against carbon tetrachloride in a spectrophotometer at a wavelength of 520 m μ .

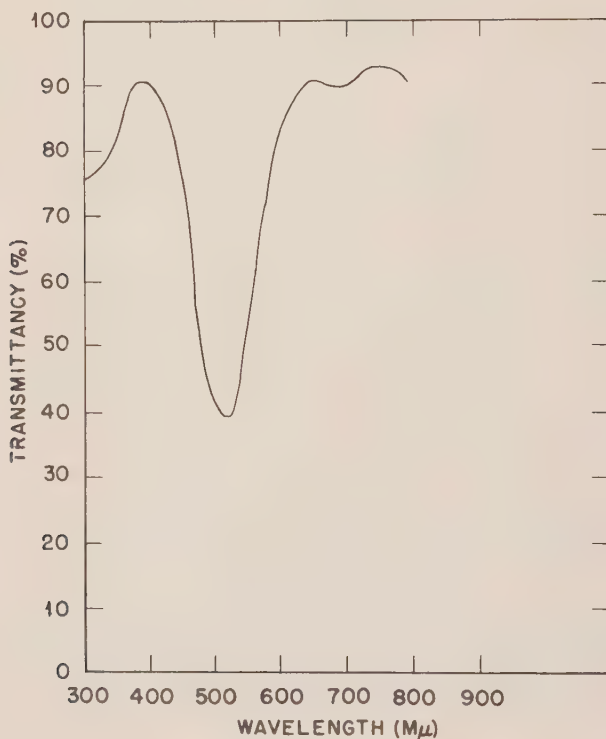


Fig. 2.3—Spectral transmittancy curve of iodine in carbon tetrachloride. Solutions were measured against carbon tetrachloride with a Coleman model 11S spectrophotometer.

(d) Nephelometric Method. Quantities of thorium less than 1 mg may be estimated nephelometrically as thorium iodate.³⁷ The thorium, after separation from interfering ions, is treated with an excess of potassium iodate and compared with standards prepared similarly. The method is rapid and is suited to certain routine work.

Procedure.³⁷ The thorium solution, freed of interfering ions and sulfates and containing not more than 1 mg of thorium, is precipitated

with ammonia, filtered, washed, and dissolved in 6 ml of HNO_3 (1 to 1). The nitrate solution is diluted to 42 ml, and 8 ml of 7.5 per cent KIO_3 is added. It is allowed to stand 15 min (30 min for less than 0.1 mg of thorium) and is matched against a series of similarly prepared standards that contain known amounts of thorium. The beakers are placed on a dark plate in front of a window and viewed from above.

(e) Other Methods. The spectrum of thorium is too complex to permit an easy spectrochemical determination of the element. The thorium content of a mineral may be determined by a study of the radioactivity of the sample. This method has been applied primarily to the analysis of rocks in which the quantity of thorium is very small. Details of the methods are described in the literature¹⁰⁰⁻¹⁰³ and in Chap. 28 on "Radiochemical Analytical Methods."

(f) Determination of Free Thorium. Elementary thorium, in the absence of other free metals, is most easily determined by the hydrogen-evolution method, using hydrochloric acid. Indirect methods involve the determination of thorium oxide in the metal by vacuum fusion or by weighing the residue from the acid treatments.

5. SELECTED PROCEDURES

The selected procedures that follow are those that illustrate the main features of the previous sections of this chapter. The methods that have been selected are used in the field of ore and mineral analysis. By analyzing these materials the solution of the sample, which may consist of complex minerals, the separation from various interfering elements, and the determination of the thorium are well illustrated.

5.1 Gravimetric. (a) Phosphate-Hexamine-Peroxide Method (in Monazite Sand). The following method was developed originally as a means of analyzing monazite sand in the total elapsed time of 4 to 6 hr. In this method titanium is precipitated along with the thorium, and a correction must be made for it. However, it has been found that this method agrees with the longer methods for determining thorium in monazite sand.

Procedure.²⁹ Ten grams of ground sand (100 mesh) is treated with 25 ml of H_2SO_4 and heated for 1 hr, with occasional stirring, in a covered platinum dish on a hot plate. The hot plate was hot enough to cause H_2SO_4 to fume strongly. The mixture is cooled and poured onto ice in a 250-ml beaker. The dish is washed with water, and the solution is stirred until the mass is completely broken up. The contents of the beaker are poured into a 250-ml volumetric flask and diluted to volume. The solution is mixed well and filtered through a Whatman

No. 42 12.5-cm filter paper, the first 15 to 20 ml is discarded, and enough filtrate is collected in a dry flask for several 50-ml aliquots.

A 50-ml aliquot is placed in a 600-ml beaker and diluted to 450 ml (pH 0.6 to 0.7). The solution is heated to the boiling point and stirred constantly to prevent bumping. Fifteen milliliters of 5 per cent sodium pyrophosphate is slowly added, and the solution is again brought to a boil for a minute or so. The precipitate is allowed to settle and is filtered with S & S 589 white ribbon 11-cm paper. The precipitate is washed off the paper back into the beaker with a stream of water. Thirty milliliters of NaOH (1 to 1) and about 1 g of Na_2O_2 are added to the slurry, which is then diluted to 200 ml and boiled 3 to 4 min. After diluting to about 400 ml, the precipitate is allowed to settle and is filtered back through the same paper from which it was washed. It is dissolved off the paper with a little hot HCl (1 to 1), the paper is washed with hot HCl (1 to 9), and the solution is collected in the original beaker. The sodium hydroxide precipitation is repeated, and the precipitate is again dissolved with HCl.

The solution is diluted to about 200 ml, and NH_4OH is added until a faint cloud appears. The HCl is added drop by drop until the solution just clears. Two to three milliliters of 5 per cent NaNO_2 and 10 g of NH_4Cl are added, and the solution is heated to about 60°C . A 2 per cent solution of hexamine is added drop by drop with stirring until the solution becomes cloudy, and 4 ml is added in excess. After allowing the precipitate to settle, 1 ml of hexamine solution is added to test for complete precipitation. The solution is heated to about 70°C , and the precipitate is allowed to settle and is filtered on a Whatman No. 40 filter paper. It is dissolved off the paper with hot HCl (1 to 1), and the paper is washed with HCl (1 to 9). The hexamine precipitation is repeated, the precipitate is dissolved with hot HNO_3 (1 to 2), and the paper is washed with HNO_3 (1 to 9).

The solution is transferred to a 250-ml beaker and diluted to 100 to 125 ml, and 10 ml of 30 per cent H_2O_2 is added. Using a pH meter to follow the change the pH is raised to 1.0 to 1.5 with NH_4OH , and the solution is heated to about 50°C . The precipitate is filtered and redissolved with HNO_3 (1 to 2) (about 10 ml). Ten milliliters of 30 per cent H_2O_2 is added, the solution is diluted to 100 ml, and the amount of TiO_2 that is present is determined by measuring the transmittancy of the solution at $400\text{ m}\mu$ and comparing it with a standard curve made under the same conditions. The pH of the solution is again raised to 1.0 to 1.5 with NH_4OH ; after warming, the precipitate is quantitatively transferred to a Whatman No. 40 9-cm filter paper and 2 per cent NH_4NO_3 is used to wash out the beaker. The precipitate is ignited at 1000°C in a platinum crucible, and the weight of the final material is corrected for TiO_2 .

(b) Hydroxide-Fluoride-Peroxide Method. The following procedure is designed to handle ores that contain about 0.04 per cent of ThO_2 and up.

Procedure.¹⁰⁵ A 5-g sample that is finely powdered is fused with about 3 g of Na_2O_2 in a porcelain crucible. The melt is disintegrated with 180 ml of warm water, after which it is neutralized with HNO_3 (1 to 1), and a few milliliters is added in excess. The crucible is removed and rinsed, and the rinses are added to the solution. The solution is cooled to about 50°C .

One milliliter of 30 per cent H_2O_2 is added to the above solution, and the thorium is precipitated with 50 per cent NaOH solution, 10 ml in excess being added. The mixture is digested on the steam bath a few minutes, cooled, filtered, and washed thoroughly with warm 0.1 per cent NaNO_3 .

The precipitate is transferred from the filter to the original beaker, and any residue that remains on the filter is dissolved with 15 ml of warm HNO_3 (1 to 1). The paper is washed with water and reserved. The solution is boiled gently for about 5 min to destroy most of the peroxide. It is then diluted to 190 ml with water and cooled, and NH_4OH is added until a precipitate forms which clots; too great an excess of ammonia must be avoided (1 or 2 drops in excess should be sufficient). Three drops of 0.1 per cent methyl red in alcohol is added, and the solution is neutralized very carefully with HNO_3 (1 to 50) until the methyl red color is just yellow or just under salmon pink. Then the solution is heated until it just starts to boil; the heat is removed, and, after the precipitate settles, the acidity is checked as indicated by methyl red color and adjusted if necessary. The solution is filtered and washed with 0.1 per cent NH_4NO_3 .

The precipitate is dissolved off the filter with 15 ml of warm HNO_3 (1 to 1), and the filter paper is washed thoroughly with water and reserved. The ammonia precipitation is repeated as above.

The paper is unfolded, and the hydroxide precipitate is transferred with a little water to a platinum dish. The filter paper is combined with those reserved from the above precipitation, the filter papers are ashed, and the ash is added to the dish containing the major precipitate. The volume of the solution at this point should be about 15 to 25 ml.

Ten to fifteen milliliters of HF is added, the dish is covered with a platinum cover, and the solution is digested on the steam bath for at least 1 hr and stirred occasionally. The sample is allowed to stand $\frac{1}{2}$ hr at room temperature.

The solution is filtered on a Whatman No. 40 filter paper through a hard-rubber funnel, and the paper is washed once with dilute HF and twice with water. The precipitate is transferred to a platinum cru-

cible, the crucible is covered loosely with a platinum cover to allow access of air, and the precipitate is burned carefully at low heat.

As little $K_2S_2O_7$ as will dissolve all the precipitate (1 g or less, depending on the size of the fluoride precipitate) is added and fused carefully until a clear melt is obtained. Care should be taken during the fusion to avoid a vigorous reaction and consequent loss of thorium by spattering. The solution is cooled, and the melt is leached with 300 ml of water that contains 10 ml of HNO_3 (1 to 1).

The solution is warmed to about $50^\circ C$, 0.5 ml of 30 per cent H_2O_2 is added, and the thorium is precipitated with 50 per cent NaOH solution, about 4 ml being added in excess. The sample is digested a few minutes on the steam bath, cooled, and filtered through a fast paper, and the precipitate is washed thoroughly with warm 0.1 per cent $NaNO_3$. This precipitation as well as the precipitation that follows is made to free the sample from sulfate.

The precipitate is dissolved off the paper with 10 to 15 ml of warm HNO_3 (1 to 1), and the paper is washed with water. The filter paper is reserved, and the precipitation with NaOH- H_2O_2 is repeated as above. The precipitate is filtered and washed with 0.1 per cent $NaNO_3$.

The precipitate is dissolved off the paper with 10 to 15 ml of warm nitric acid (1 to 1), and the paper is washed with water. The filter paper is reserved. The solution is brought to a boil and simmered gently for about 5 min to destroy the peroxide. The volume of the solution is adjusted to about 150 ml, after which the solution is cooled and NH_4OH is added in very slight excess until a precipitate forms and clots. A few drops of methyl red are added, and the solution is neutralized carefully to just yellow or just under the salmon-pink color of methyl red. The solution is heated until it just starts to boil, the heater is removed, and the precipitate is allowed to settle. The acidity is checked and adjusted if necessary. It is filtered through a fast paper and washed with 0.1 per cent NH_4NO_3 solution.

The precipitate is dissolved off the filter with 10 to 15 ml of HNO_3 (1 to 1), and the paper is washed with water. The filter paper is reserved, and the precipitation with NH_4OH is repeated in the same manner. It is then filtered and washed with 0.1 per cent NH_4NO_3 , the paper is transferred with the precipitate to a platinum crucible, and the filter papers that were reserved from the previous precipitations are added. The papers are ashed at a low heat with the crucible loosely covered.

The crucible is filled two-thirds full with HF (about 10 ml) and is covered. The mixture is digested on the steam bath from $\frac{1}{2}$ to 1 hr, the length of time depending on the size of the precipitate, and then transferred to a platinum dish by means of a stream of water, and the

crucible is thoroughly scrubbed. The volume of the solution is adjusted to 25 to 30 ml with water after which the solution is allowed to settle a few minutes and is filtered. The precipitate is washed with dilute HF and then twice with water. The precipitate is burned carefully in a covered crucible.

The fluoride precipitate is dissolved with potassium pyrosulfate as before, and two NaOH-H₂O₂ precipitations are made as before.

The final NaOH-H₂O₂ precipitate is dissolved with 10 ml of HNO₃ (1 to 1). The solution is boiled 5 min to destroy most of the peroxide and to reduce the cerium, then it is cooled, and NH₄OH is added in very slight excess so that a precipitate forms and clots. Two drops of methyl red is added, and it is neutralized with dilute HNO₃ until the color is just red. The solution is heated until it starts to boil, and the heater is removed. Five milliliters of 30 per cent H₂O₂ is added, it is stirred once, and exactly 1 ml of HNO₃ (1 to 4) is added immediately. The total volume of solution should be 100 ml. It is digested on the steam bath for 5 min, filter-paper pulp is added, and it is filtered and washed thoroughly with NH₄NO₃ wash solution. The precipitate is burned very carefully in a loosely covered platinum crucible at low heat, and the thorium oxide is weighed. The peroxynitrate precipitate of thorium tends to spatter and may be lost mechanically if the heating is hurried and the crucible is not covered.

It is seldom that another peroxynitrate precipitation is necessary, but if the precipitate is off-color instead of white, it is dissolved in 10 ml of hot nitric acid (1 to 1), the solution is boiled to remove peroxide and reduce cerium, and the thorium is reprecipitated with peroxide before igniting and weighing.

(c) Fluoride-Hexamine-Oxalate Method.²⁵ This method may be used with various types of ores and is an example of using fluoride, hexamine, and oxalate to separate thorium from interfering elements. The method is time-consuming and is not applicable to ores that contain very small amounts of thorium.

Procedure. The finely ground accurately weighed sample (about 1 g) of the ore is transferred to a 30-ml platinum crucible. It is moistened with a little water, about 20 ml of 48 per cent HF is added, and the sample is evaporated to dryness on a steam bath. The treatment is repeated if the sample contains much silica. After the HF treatment, about 10 g of dried KHF₂ is added to the crucible, which is covered and placed over a very low flame until the moisture and reaction gases are carefully driven off. The flame is gradually increased until the melt is a clear, red-hot molten mass using the full flame of a Meker burner. The melt is swirled to mix the fusion mass, but care must be used throughout the fusion because the material

tends to foam, creep, and sputter. When cool, the melt is swirled to form a thin coating on the sides of the crucible. When the crucible is cool it is placed in a large platinum dish, and about 200 ml of water and 25 ml of 48 per cent HF are added. The melt is removed from the crucible and broken up with a platinum rod. After the melt has digested on a steam bath for 1 hr, it is cooled, filtered through a Whatman No. 42 filter paper, and washed with dilute HF and finally with water. The residue is ignited at 450 to 500°C and transferred to a platinum dish with the aid of 15 ml of H_2SO_4 and a little cold water. The solution is evaporated to fumes and then cooled. The sides of the dish are washed down with water, and the solution is again taken to fumes. After the mixture has cooled about 100 ml of water is added, and it is stirred and digested on the steam bath to dissolve the solids.

The solution is transferred to a 400-ml beaker. If some insoluble material remains in the platinum dish it is dissolved in warm HCl (1 to 1) and added to the beaker. Usually, all the material is soluble at this point, but if some insoluble residue remains, it will dissolve after the addition of ammonia and sodium nitrite. The solution is nearly neutralized with ammonia, and a 10 per cent solution of sodium nitrite is slowly added to reduce cerium(IV) to cerium(III). If cerium is present the solution will probably be very yellow, and the addition of sodium nitrite will give a clear liquid unless iron or some other colored ion is present. Ammonium hydroxide is added until there is a 10 per cent excess. The solution is allowed to cool and settle before it is filtered through a Whatman No. 40 filter paper, and it is washed with a little cold 2 per cent NH_4Cl –10 per cent NH_4OH solution. The precipitate is dissolved on the paper with hot HCl (1 to 2), and the solution is returned to the original beaker. If the precipitate is large it may be necessary to remove the paper from the funnel and slurry with 10 to 15 ml of hot HCl (1 to 1) in a small beaker. This solution is filtered into the original beaker, and the paper is washed well with hot 5 per cent HCl.* To the combined filtrates and washings, ammonium hydroxide (1 to 1) is added until a faint permanent turbidity or precipitate is formed, and then a few drops of HCl (1 to 1) are added

*If much R_2O_3 other than thoria is present, it is advisable either to remove the iron by an ether extraction or to make an oxalate precipitation at this point. To extract the iron, the ammonia precipitate is dissolved with hot HCl (1 to 1), cooled, and shaken with ether. The oxalate precipitation is a longer procedure. The HCl solution of the dissolved ammonia precipitate is evaporated to dryness, and the method for oxalate precipitation given above is followed. The oxalates are ignited at 500°C for at least 2 hr, dissolved in hot concentrated HNO_3 , diluted, and precipitated with ammonium hydroxide. The precipitate is dissolved with hot HCl (1 to 1), and the procedure is continued with the hexamine separation. If nitric acid does not dissolve the ignited oxalates, a pyrosulfate fusion is necessary.

to dissolve the precipitate. The solution is diluted to 200 ml, and enough NH_4Cl is added to make a 5 per cent solution of the salt. One-half to one milliliter of 10 per cent sodium nitrite is added, and the solution is stirred well and warmed to about 60 to 70°C. A 2 per cent hexamine solution is slowly added until a turbidity is just produced, then 3 to 4 ml more is added. The solution is stirred well and heated to not over 75°C to coagulate the precipitate and allow it to settle. One milliliter more of hexamine solution is added to the clear liquid to see whether precipitation is complete. If more precipitate forms, more hexamine is added in 1-ml portions until no more precipitate forms. After the precipitate has settled it is filtered through a Whatman No. 40 filter paper* and washed with 5 per cent NH_4Cl . The filtrate is tested for complete precipitation by adding 1 ml of hexamine solution. The precipitate is dissolved on the paper with hot HCl (1 to 2), and the paper is washed with hot 5 per cent HCl . The hexamine precipitation is repeated twice or until the filtrate from the precipitation gives no precipitation when it is made strongly ammoniacal.

The final precipitate is dissolved as before and collected in a 250-ml beaker. The solution is evaporated to dryness on the steam bath, and 20 to 25 ml of 10 per cent oxalic acid is poured onto the residue. This is stirred and then diluted to 100 ml. The beaker is covered, and the solution is boiled gently for a few minutes and then left to stand overnight. The precipitate is filtered through a Whatman No. 42 filter paper, washed with 1 to 2 per cent oxalic acid, ignited at 1100°C, cooled, and weighed as ThO_2 .

(d) Iodate-Oxalate Method.¹⁰⁴ This method, as given, is for application to monazite sand, but it can be adapted to other ores as well. It is an example of the use of iodate to achieve a separation from the rare earths.

Procedure. A 5-g sample is accurately weighed into a silica evaporating dish and treated with concentrated H_2SO_4 , so that there is 8 ml of acid for every 5 g of monazite. Products that are not broken down with H_2SO_4 should be fused with NaHSO_4 , KHF_2 , or alkali. The mixture is stirred with a glass rod, and the dish is covered with a watch glass and heated on a sand bath to just below 200°C. The heating is continued for 2 hr with frequent stirring. Care must be taken to avoid spattering, boiling of H_2SO_4 , or overheating.

The dish is cooled, and ice-cold water, in the amount of 50 to 60 ml for each 5 g of monazite, is added with constant stirring. The turbid liquor is decanted into a 400-ml beaker, and the heavy-mineral resi-

*It is best to place a pad of macerated filter paper in the apex of the filter paper when filtering all precipitates that are encountered in this method.

due is treated with concentrated H_2SO_4 (2 ml for each 5 g of monazite) and heated as before for 3 hr. The dish is again cooled and cold water is added as before. All the material is washed into the 400-ml beaker and stirred thoroughly to dissolve all soluble salts. The solution is warmed to about 40°C , and 0.5 ml of a 1 per cent solution of gelatin is added. More gelatin solution may be added if the solution does not clear on stirring and standing. The solution is filtered through a Whatman No. 42 filter paper, and the residue is washed thoroughly with water. This residue is worked up, if it is necessary to do so, by the following operations: The insoluble residue of silica and mineral is transferred to a platinum dish and calcined. It is mixed with about three times its weight of KHF_2 , brought to fusion, and stirred with a platinum wire. After cooling, 2 ml of H_2SO_4 is added and fumed strongly. Any insoluble residue is then fused with Na_2CO_3 , leached with water, and made acid with H_2SO_4 . Any precipitate is filtered, and the H_2SO_4 extracts are added to the main solution.

The solution should now be about 100 ml if 5.0 g of monazite has been taken. If larger samples are used, the solution is made up to volume in a graduated flask of such size that 100 ml of the resulting solution could contain the equivalent of 5 g of sample. To the 600-ml beaker that contains the clear solution of about 100 ml is added 50 ml of HNO_3 with stirring. If ceric salts are present these should be reduced to cerous by adding H_2O_2 to the acid solution before iodate precipitation. In another beaker, 16 g of KIO_3 is dissolved in 50 ml of concentrated HNO_3 and 30 ml of distilled water. The iodate solution is added to the acid solution of monazite slowly and with continuous stirring. The beaker is covered with a watch glass and cooled in ice water to room temperature. The cold mixture is filtered through a toughened paper (Whatman No. 541). This paper is used for each filtration up to the oxalate filtration. The filtrate should be very clear. The last traces of iodate are washed onto the paper with 30 to 50 ml of a wash solution that contains 8 g of KIO_3 , 50 ml of HNO_3 , and enough distilled water to make 1 liter. The precipitate is allowed to drain thoroughly, and then the paper is carefully removed from the funnel and opened over the beaker in which the precipitation was carried out. Every trace of the iodate deposit is washed off the paper with 50 to 100 ml of the iodate wash solution. The precipitate and wash solution are stirred to break up thoroughly any lumps that may be present. The mixture is filtered through the same paper, washed onto the paper, and allowed to drain as before. Again the deposit is washed back into the beaker off the opened paper with 50 to 100 ml of distilled water. The water suspension is heated and kept nearly at the

boiling point, while HNO_3 is added until the solution is clear and free from precipitate. The HNO_3 is added in small quantities at a time, and amounts of between 30 to 90 ml are normally required (60 ml for 0.5 g of ThO_2). A solution of KIO_3 is prepared in boiling water such that 8 g of KIO_3 is present for every 60 ml of HNO_3 that is used to dissolve the precipitate. The KIO_3 is added to the hot thorium iodate solution with brisk stirring. The beaker is cooled to room temperature in ice water. The precipitate is filtered, washed off the paper, and refiltered as was done with the first iodate precipitation. The precipitate is again washed into the beaker, and both sides of the paper are thoroughly washed with water. The volume of suspended deposit should be about 100 ml.

The suspension is warmed to about 40°C , and 25 ml of HCl is added. Sulfur dioxide gas is passed from a cylinder into the suspended thorium iodate mixture until a clear, faintly yellow solution smelling of SO_2 is produced. The mixture is first dark brown owing to free iodine, but the solution clears rapidly. The clear solution is filtered through the same filter paper that was used before, and care is taken to make certain that any iodate left on or in the paper is removed. (No brown stains due to iodine should be left on the paper.) The filtrate is again passed through the paper and then washed thoroughly with distilled water. About 200 ml of water should be used. The well-stirred filtrate and washings are made alkaline with strong ammonia solution. A white hydroxide separates, and the mixture is allowed to stand for 1 hr. The solid is then filtered on the same paper as previously used, and the filtrate is tested with ammonia to make certain that no thorium remains. The precipitate is washed with 50 to 100 ml of ammoniacal NH_4Cl (5 per cent NH_4Cl plus a few drops of 0.880 NH_4OH). Twenty-five milliliters of HCl is added to 100 ml of distilled water, and this acid is poured through the filter to dissolve the thorium hydroxide. The filtrate is refiltered through the same paper, and then the paper is well washed with hot distilled water. The filtrate and washings (about 400 ml) are raised to the boiling point, and a boiling solution of 25 g of oxalic acid in 200 ml of water is slowly added with constant stirring. The oxalate precipitate is stirred and allowed to cool and stand overnight (12 to 16 hr).

The thorium oxalate is filtered through a fresh Whatman No. 42 filter paper and washed with distilled water (about 50 ml), and care is taken to make certain that all precipitate has been removed from the walls of the beaker. The last traces may be removed with a small piece of filter paper. The wet paper with oxalate precipitate is placed in a weighed platinum crucible, and the mixture is carefully heated so

that the product chars but does not ignite. After fumes have ceased, the product is heated for 2 hr at 900 to 1000°C, cooled, and weighed to constant weight.

(e) Determination of Traces in Ores.³⁷ The following procedure, which is essentially the chemical concentration of thorium, has been used in a variety of ores and minerals of all types. After the thorium has been concentrated, it may be determined by several methods. These methods include the colorimetric method with pararsonic acid, the nephelometric method with the iodate, and the gravimetric method which uses precipitation with ammonia and peroxide. The gravimetric method is preferred when more than 1 mg of thorium is present.

Procedure.³⁷ For samples containing less than 0.04 per cent thorium a 5-g sample is taken, and proportionally less is taken for higher thorium content. For samples with a total radioactivity count equivalent to 0.015 per cent uranium or less a 5-g sample is taken. The sample is ground to pass a 60- to 80-mesh screen and is weighed. If it contains organic matter or sulfides it is ignited at top heat of a Meker or Fisher burner. It is then digested in a covered platinum dish on the steam bath for 30 min with 40 ml of HNO_3 (1 to 1). The cover is removed, 10 to 15 ml of HF is added, and the solution is slowly evaporated to dryness on a steam bath. If there is much unattacked material the digestion with acid is repeated. The sample is evaporated to dryness twice more with HNO_3 . The dry residue is transferred to a porcelain or glass container, the platinum dish is rinsed with HCl (1 to 1), 10 ml of HCl is added, and the solution is evaporated to dryness. This is followed by two more evaporations to dryness with HCl. The residue is digested with 20 ml of HCl (1 to 1) while covered, the solution is filtered, and the residue is washed with hot HCl (1 to 1) and finally with a little hot water. The residue is then ignited in platinum, a little HF and 1 drop of H_2SO_4 are added, and the solution is evaporated to dryness. The remaining residue is sintered with as little Na_2CO_3 as possible and dissolved in HCl (1 to 1). If there is any unattacked residue, it is filtered and sintered with Na_2CO_3 and dissolved in HCl (1 to 1).

If much SiO_2 separates when the fusion mass is treated with HCl (1 to 1), the solution is evaporated to dryness in platinum and treated with HF and a few drops of H_2SO_4 , and the solution is fumed. The residue is then taken up in HCl (1 to 1) and added to the main sample. If little or no SiO_2 separates when the HCl is added, the solution is added to the previous filtrates. The combined filtrates are evaporated to about 25 ml. Any hydrolytic precipitate should be left in the solution, or, if filtered, it should be added to the phosphate precipitate when it is burned. The solution is evaporated to dryness to eliminate

the free acid, and then 10 ml of HCl (1 to 1) is added. The solution is digested for about 5 min on the steam bath, and 130 ml of water is added. The contents of the beaker are digested on the steam bath until soluble salts are dissolved. While stirring, 10 ml of zirconium nitrate solution [$1.05 \text{ g ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to 100 ml of water] is slowly added, and the solution is warmed to about 90°C . Four grams of diammonium phosphate dissolved in about 20 ml of water is added, and the solution is diluted with water to 200 ml. The beaker is covered and its contents are digested on the steam bath for at least 4 hr. Paper pulp is now added, and the solution is stirred and filtered on an S & S 589 white ribbon 11-cm paper. The precipitate is then washed with a 4 per cent ammonium nitrate solution. The filter paper and precipitate are transferred to a porcelain crucible and gradually heated until the carbon is burned off. The residue is transferred to a 100-ml platinum dish or crucible and moistened with a little water, and 20 ml of HF is added. The dish is covered with a platinum cover and digested until the precipitate is in solution, and the solution is evaporated on the steam bath until about 8 ml remains. Ten milliliters of HF is now added, and the solution is evaporated again to about 8 ml and then diluted with 30 ml of water. The solution is warmed on the steam bath, and 10 ml of mercurous nitrate solution is added. (The mercurous nitrate solution is prepared by dissolving 0.952 g of $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ in 100 ml of water that contains a few drops of HNO_3 .) Ten milliliters of dilute HCl (7 to 100) is added, and the solution is stirred with a platinum rod. The solution is warmed on the steam bath for a few minutes and then allowed to stand at room temperature for about 4 hr. After this time it is filtered on a Whatman No. 40 9-cm filter paper in a hard-rubber funnel. The precipitate is washed twice with 10 to 15 ml of 5 per cent HF wash solution, the wash solution being made directly in the dish that contains the precipitate, and the inside of the dish is scrubbed thoroughly with a rubber policeman. The precipitate is then washed twice with water. The paper and precipitate are transferred to a 20-ml platinum crucible, well shielded from drafts, and burned gently below 500°C in a well-ventilated hood until the paper is burned off and the HgCl is volatilized. The precipitate must be burned carefully and slowly, because if the mercurous chloride is volatilized too fast thorium may be lost by dusting. Burning at too high a temperature may convert some of the thorium fluoride to ThO_2 , which is harder to dissolve. The fluoride residue is carefully moistened with a few drops of water, and about 8 ml of HF is added. The crucible is covered, and the contents are digested on the steam bath for 20 min. The material is transferred to a platinum dish, and the inside of the crucible is wet and

thoroughly scrubbed with a rubber policeman. The solution is diluted with water to 40 ml, 10 ml of the mercurous nitrate solution is added, and the mixture is warmed. One milliliter of dilute HCl (7 to 100) is added, and the solution is stirred and allowed to stand at room temperature for about 4 hr. It is then filtered on a Whatman No. 40 9-cm filter paper on a hard-rubber funnel and washed twice with HF wash solution and twice with water. The paper and precipitate are transferred to a 20-ml platinum crucible and again carefully burned below 500°C in a well-ventilated hood until the paper is burned off and the HgCl is volatilized. The residue in the crucible is carefully wet with a few drops of water and dried on a steam bath; then 0.5 ml of H_2SO_4 is carefully added, and the crucible is heated on the hot plate for about 15 min after fumes have appeared. The solution is cooled, and water is added cautiously until the crucible is about three-fourths full.

A few drops of sulfurous acid solution are now added to decolorize any quadrivalent cerium, and the solution is evaporated to fumes and kept fuming for 15 min. After it has cooled, about 10 ml of water is added, and the contents are transferred to a 50-ml beaker. The crucible is polished and washed with water, and the washings are added to the beaker. At this point the volume of the solution should be 25 to 30 ml. The solution is warmed gently and then allowed to stand for about 4 hr. The dilution with water and the fuming with sulfuric acid should be repeated a third time if the amount of thorium is large or if the final insoluble residue is large. Any lead sulfate is filtered off on a Whatman No. 42 7-cm filter paper and washed a few times with H_2SO_4 solution (1 to 99). The filtrate is collected in a 50-ml platinum dish and evaporated to fumes, and the sulfuric acid is driven off at a low temperature. This is conveniently done by heating on a hot plate until dry and then rotating the dish over a low bunsen flame until no more fumes appear. The temperature should be kept below 450°C to avoid formation of ThO_2 , which, in the next step, may not dissolve completely in the HNO_3 . The removal of free sulfuric acid is essential since excess sulfate interferes with the precipitation of thorium iodate. To the solution is added 6 ml of HNO_3 (1 to 1) from a pipet, and then 1 drop of 30 per cent hydrogen peroxide is added. After the mixture has been warmed gently, 10 ml of water is added, and the mixture is digested on the steam bath for a few minutes until the thorium is dissolved. The solution is transferred to a 100-ml beaker by means of a jet of water, and the dish is polished thoroughly. The volume of solution is adjusted to 42 ml (the beaker should be marked at the 42-ml level before the solution is added) and is then cooled to

room temperature, and 8 ml of a KIO_3 (7.5 g KIO_3 in 100 ml of H_2O) solution is added. The thorium may now be determined (1) nephelometrically as the iodate when less than 1 mg of ThO_2 is present (Sec. 4.3d); (2) photometrically with pararsonic acid (Secs. 3.1j and 4.3a); or (3) gravimetrically as the oxide if more than 1 mg of ThO_2 is indicated by the size of the iodate precipitate.

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Chapter 3

NITROGEN

By K. J. Jensen and R. J. Mundy

In one connection or another, occasion arose for the determination of nitrogen in its various states of oxidation in compounds and mixtures. Semimicro and micro modifications of the Kjeldahl procedure were utilized extensively. Final measurements were made either by titration or by colorimetric determination with Nessler's reagent. In many instances the free nitric acid content of uranium and thorium nitrate solutions was required.

The micro-Kjeldahl method¹ was most commonly used for the determination of nitrogen in uranium samples.²⁻¹¹ This method was applied successfully to thorium samples also. The results obtained are consistent, and correlation with results from the vacuum-fusion method has been fair.¹² The separated ammonia may be either titrated or determined colorimetrically with the use of Nessler's reagent.^{7,13} The volumetric method may be used over a wider range. However, the colorimetric method is more rapid for routine work and has been found to give results that are sufficiently accurate.

The vacuum-fusion procedure requires considerable time and special equipment. Fairly consistent results may be obtained by dropping samples of low nitrogen content into outgassed molten steel.¹²

A modified Dumas method using potassium chlorate as a source of additional oxygen has been used for uranium nitride samples.¹⁴

A method for the determination of nitrate nitrogen has been developed in which the nitrate is converted to ammonium sulfate by using a combination of sodium sulfite, chromium sulfate, mercuric oxide, and zinc metal.¹⁵ After reduction the solution is distilled in a micro-Kjeldahl flask, and the ammonia is collected in a standard acid solution. The excess acid is then titrated. A similar method on a macro scale employing aluminum as a reducing agent has also been used.¹⁶

The determination of nitric acid in solutions containing uranyl and thorium nitrate has been widespread on the Project, adaptations of standard methods being used. One method, employing a modification of a standard procedure,¹⁷ removes chloride and metal ions by means of silver oxide before titrating with ferrous sulfate.

Sturtevant¹⁸ suggested an empirical method for the determination of nitric acid in uranyl nitrate, based upon titration with sodium hydroxide.¹⁹ In an improvement on this method²⁰⁻²² the uranium is precipitated with hydrogen peroxide. The hydrogen ion formed by the uranium peroxide reaction is titrated along with any free acid in the solution.

Hammond and Parlour²³ precipitated the uranium in uranyl nitrate solution with potassium ferrocyanide. The nitrate from uranyl nitrate combines with the potassium to form a neutral salt. In this way only the free nitric acid remains to be titrated. A modification of this method²² was employed for the analysis of aqueous and ethereal solutions of uranyl nitrate.

Nitric acid has been determined in organic solvents by titration with *n*-amylamine dissolved in dibutyl carbitol using bromphenol blue or sodium thiocyanate as indicators.²⁴

Conductimetric titration with sodium hydroxide has been used to determine nitric acid in thorium nitrate solutions.²⁵

Other conventional methods were the determination of nitrate nitrogen using phenoldisulfonic acid^{13,26} or using indigo carmine.^{27,32} For the colorimetric determination of nitrite nitrogen in water a mixture of sulfanilic acid and naphthylamine was used.^{13,26}

1. METHODS OF SOLUTION

Uranium metal may be dissolved in phosphoric acid, but the action is slow. Hydrochloric acid is satisfactory in spite of the fact that some insoluble material remains. Earlier procedures called for the use of concentrated hydrogen peroxide solution to aid in dissolving the residue. Careful investigation indicated that the use of the peroxide might be omitted.²⁸ The use of peroxide for this purpose may cause loss of nitrogen, and it frequently causes a high reagent blank.

Hydrochloric acid may be used for the solution of thorium. In this case the insoluble residue may retain nitrogen to the extent of 30 ppm for samples of 500-ppm nitrogen content. If the insoluble residue is heated with hydrochloric acid and sodium fluosilicate, all the nitrogen is brought into solution.¹¹

The Dumas method requires no solution of the sample, since the material is burned and the nitrogen is volatilized as a gas.

Organic nitrogen compounds may be put into solution by digesting with hot sulfuric acid in the presence of a catalyst. This method was found to give low results for nitrogen in uranyl cupferrate. These results were to be expected because of the presence of the nitroso group,¹ whereas the Dumas method was satisfactory.

2. DETERMINATION OF NITRIDE NITROGEN

2.1 Volumetric Micro-Kjeldahl Method for Uranium and Thorium Metal. The sample is dissolved in hydrochloric or phosphoric acid and added to an excess of sodium hydroxide. The ammonia is steam-distilled, collected in a flask containing a 2 per cent boric acid solution, and titrated with 0.01N HCl, using a mixed indicator. A modified commercial Parnas and Wagner micro-Kjeldahl distillation apparatus¹ is used. The conventional apparatus is modified slightly by substituting stopcocks of wider bores (4 and 6 mm, respectively) at the top and bottom of the discharge compartment in order to prevent clogging.

Procedure.^{7,34} A sample weighing from 2.5 to 4.0 g is taken. It is prepared for solution by boiling in 15 per cent sodium carbonate, rinsing in distilled water, and immersing for several minutes in hot 5 per cent HCl. After cleaning, the sample is dried, weighed, and put in an Erlenmeyer flask. A blank on reagents is also run through the entire procedure. Ten milliliters of constant-boiling hydrochloric acid is added to the blank and sample. While the sample is dissolving, the distillation apparatus should be thoroughly steamed out. When the apparatus has cooled somewhat from the steaming process, 10 ml of 50 per cent NaOH is washed into the distillation flask. The flame is applied to the steam generator. The stopcock at the top of the safety trap is closed, and the stopcock at the bottom is opened to equalize the pressure. A receiving flask containing 5 ml of 2 per cent boric acid solution and 4 drops of mixed indicator (5 parts of a 1 per cent alcoholic solution of bromcresol green and 1 part of a 1 per cent alcoholic solution of methyl red) is placed under the condenser tip. The tip of the condenser should be below the surface of the liquid. The solution of the sample in the Erlenmeyer flask is swirled in order to loosen the fine-grained precipitate and is transferred to the distillation flask with washing. The stopcock of the separatory funnel is closed, the stopcock at the top of the safety trap is opened, and the one at the bottom of the trap is closed. Steam now passes into the distillation flask. The distillation proceeds until 20 to 25 ml of distillate has been collected in the receiving flask. Toward the end of the run the receiving flask is lowered, the tip of the condenser is washed, and the distillation is continued for 1 min. After the dis-

tillation is complete, the flask is removed and titrated with standard 0.01N HCl. The spent solution is removed immediately after each run by turning off the heat under the steam generator and running in cold distilled water from the reservoir. (The reservoir should contain a few milliliters of H_2SO_4 .) It is then discharged by opening the stop-cock at the bottom of the trap.

The apparatus should be cleaned after all runs have been completed, using a mixture of 10 per cent HCl and a few milliliters of 30 per cent H_2O_2 . The solutions are mixed and added to the still. A pyrex tube is substituted for the silver condenser, since silver is attacked by nascent chlorine. Steam is passed through the apparatus for a few minutes, and then the cleaning solution is removed. A thorough steaming should follow this cleaning procedure.

2.2 Colorimetric Micro-Kjeldahl Method.⁷ Nitrogen is separated as ammonia by distillation. The ammonia is collected in a dilute hydrochloric acid solution, and Nessler's reagent is added to develop the color. The solution is diluted, and the color is compared with a permanent set of standards.

The distillation apparatus is the same as that used above. The color is observed in high-form Nessler tubes.

The preparation of Nessler's reagent is described in standard methods for water analysis.¹³ The permanent standards are prepared by using a mixture of varying amounts of three solutions, potassium chloroplatinate, cobaltous chloride, and nickel chloride, and diluting to 50 ml. These solutions are made by dissolving 2.0 g of potassium chloroplatinate, 12.0 g of anhydrous cobaltous chloride, and 6.0 g of nickel chloride hexahydrate in separate 100-ml portions of concentrated hydrochloric acid and diluting each to 1 liter. The mixtures of these solutions and the corresponding micrograms of nitrogen represented by each solution appear in Table 3.1.

The distillation procedure is essentially the same as in the above method except that the distillate (40 to 50 ml) is caught in an Erlenmeyer flask containing 10 ml of distilled water and 1.0 ml of 0.01N hydrochloric acid. One milliliter of Nessler's reagent is added, and the color is allowed to develop for 15 min. The colored solution is then transferred to a Nessler tube and diluted to 50 ml, then mixed and compared with the artificial permanent standards.

2.3 Macro-Kjeldahl Method for Uranium Metal. The conventional macro apparatus has been used.²⁹

Procedure. To an approximate 10-g sample in a 1-liter Kjeldahl flask is added 30 ml of distilled water and 30 ml of HCl. When the action has ceased, the contents of the flask are heated in a steam bath for 30 to 45 min. The solution is cooled and diluted with 300 ml of

redistilled water, several large glass beads are added, and 60 ml of NaOH (50 g per 100 ml of redistilled water) is slowly poured down the sides of the flask. The solution is boiled until 200 ml of the distillate has passed over. The distillate is collected in a 500-ml Erlenmeyer flask containing 30 ml of redistilled water, 10 ml of 0.01N H_2SO_4 (1 ml equivalent to 140 γ of nitrogen), and 4 or 5 drops of mixed indicator (prepared by dissolving 1.2 g of methyl red and 0.82 g of methylene blue in 1 liter of 90 per cent ethyl alcohol). The excess acid is titrated with 0.01N NaOH until the first appearance of a clear bright green. A blank is run with every set of samples.

Table 3.1 — Volumes of Permanent Standard Solutions Necessary to Match Colors of Ammonium Chloride Standards

Nitrogen, γ	Cobalt solution, ml	Potassium solution, ml	Nickel solution, ml
2*	0.15	1.7	
4*	0.27	2.3	3.6
6*	0.40	3.5	3.0
10	0.66	4.9	2.8
14	0.90	6.6	3.7
17	1.2	7.4	3.7
20	1.7	9.0	6.0
25	2.4	11.0	6.2
30	3.2	14.6	9.2
35	3.7	14.8	11.7
40	4.5	13.3	10.6
50	5.7	15.3	15.4
60	8.4	23.7	18.0
70	8.6	17.3	12.5

*These standards match solutions containing the corresponding amounts of nitrogen, in which the color has been developed before dilution. The color does not develop with less than 10 γ in 50 ml volume.

3. METHODS OF DETERMINATION OF NITRATE NITROGEN

3.1 Micro Reduction Method. In this modification of a published method³⁰ nitrate is reduced to ammonia by boiling in sulfuric acid, using sodium sulfite, chromium sulfate, mercuric oxide, and zinc metal. The ammonia is distilled into standard acid in a micro-Kjeldahl distillation apparatus, and the excess acid is titrated. Any ammonium or nitrogen compounds that are converted to ammonia will also be determined by this procedure. These must be either removed or de-

terminated by running a blank. The range of the method is from 25 γ to 10 mg. The recovery is 99 per cent or better on quantities of 100 γ or more, and above 95 per cent on quantities less than 100 γ .

Procedure.¹⁵ The sample, containing 25 to 1,000 γ , is transferred to a micro-Kjeldahl digestion flask, and 0.5 ml of sulfuric acid and 1 ml of chromium sulfate solution [0.5 g of $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ per milliliter] is added. Next, 2.5 ml of sodium sulfite solution (0.25 g of Na_2SO_3 per milliliter) is added, and the mixture is digested for 5 to 7 min, with the evolution of sulfur dioxide fumes. When the sulfur dioxide can no longer be detected, the solution is cooled slightly, and about 0.1 g of mercuric oxide is added. This is followed by 0.75 g of zinc metal. The mixture is then heated moderately for 10 min. If a light-blue color appears, a few crystals of sodium sulfite are added to produce a deep greenish-black color, and boiling is continued for about a minute.

The digest is cooled to room temperature, transferred to a micro-Kjeldahl apparatus,^{1,31} and rinsed with 5 ml of distilled water added in three portions from a pipet. An amount of 50 per cent NaOH (about 0.5 ml in excess of the quantity needed to neutralize the concentrated sulfuric acid present) is added and rinsed in with a little water. Exactly 2 ml of the standard 0.01N sulfuric acid is placed in a 20-ml low-form beaker or a small dish, which is placed so that the acid covers the end of the condenser delivery tube. Steam is passed through the solution for 5 min after starting to condense. The receiver is lowered and the delivery tube is rinsed while distillation is still proceeding. The excess acid is titrated with a capillary buret filled with standard 0.3N NaOH. Methyl red is used as an indicator.

3.2 Indigo Carmine. A method employing indigo carmine³² has been used for determining nitrate ion concentration^{27,32} in UO_3 .

Procedure.²⁷ The sample (0.1 to 0.5 g) is weighed and transferred to a 50-ml Erlenmeyer flask. To this is added 15 ml of indigo carmine reagent, which is prepared by dissolving 0.4 g of indigo carmine in 1,000 ml of H_2SO_4 (1 to 20), 5 ml of HCl (1 to 1), and 17.5 ml of water. The solution is mixed well, 12.5 ml of H_2SO_4 is added, and the solution is again mixed well. It is then placed on a hot plate, boiled for 2 min, cooled, and diluted to 50 ml. The transmittancy of the solution is measured against a distilled water blank with an electrophotometer, using a blue color filter. The nitrate content is obtained from a transmittancy-concentration curve prepared by taking known amounts of nitrate through the procedure.

Blank values must be established carefully since ammonia or nitrate may be in the reagents used. This is performed exactly as in the determination except that the sample is omitted.

4. METHODS OF DETERMINATION OF NITRIC ACID AND NITRATE

The determination of nitric acid in uranyl nitrate and other solutions has been of Project-wide interest (see bibliographic references 18, 20 to 25, and 33). These methods are generally based on a determination of free acid present and are not specific for nitric acid. Since the application has been so general, several representative determinations are included in this chapter. The more recent procedures, whereby the bulk of the uranium is precipitated as peroxide^{20,21} or ferrocyanide,^{23,33} have superseded the older empirical titration method of Sturtevant.¹⁸

4.1 Peroxide Precipitation Method. When hydrogen peroxide is added to a solution of uranyl nitrate, uranium peroxide is precipitated, and an equivalent amount of nitric acid is formed in accordance with the equation



Between pH 2.0 and 5.0 this reaction is quantitative in the absence of interfering substances. The free nitric acid, together with the acid formed in the above reaction, is titrated potentiometrically at room temperature to pH 4.5 with a standard solution of sodium hydroxide. The amount of uranyl nitrate is determined either on the portion titrated or on a separate portion, and a correction is made for the amount of sodium hydroxide required to react with the uranyl nitrate. A stoichiometric factor of 2 moles of sodium hydroxide per mole of uranyl nitrate is used.

Procedure.²¹ A sample is taken of such size that the free acid, plus the acid generated from the reaction of hydrogen peroxide with the uranyl nitrate, does not consume more than 50 ml of 0.1N sodium hydroxide. The sample should not contain more than 10 g of sodium nitrate. After dissolving in water and diluting to 100 ml, 10 ml of 3 per cent hydrogen peroxide is added, and the titration is carried out potentiometrically to pH 4.5 without filtering off the precipitate. To determine the free nitric acid, a determination of the uranium content is necessary.

4.2 Ferrocyanide Precipitation Method. In some solutions containing iron, aluminum, nickel, cobalt, calcium, barium, magnesium, and sodium ions in addition to uranium nitrate and free nitric acid, it has been found that all interferences except aluminum may be removed by the use of potassium ferrocyanide. The effect of the aluminum is corrected by an extrapolation of the potentiometric titration

curve with the aid of a normal nitric acid curve for similar conditions of dilution.

The following procedure has been used on aqueous solutions and also on solutions from which the ether has been removed by evaporation.

(a) Procedure for Ether Solution.³³ The weighed or measured sample is added to about 10 ml of pure water in a flask, and the ether is evaporated off at room temperature either under moderate suction from a filter pump or by a current of air. No appreciable loss of nitric acid is incurred in this transfer to water solution. The water solution to be analyzed is placed in a 50-ml calibrated flask and treated with a relatively large volume of saturated potassium nitrate solution, followed by potassium ferrocyanide in excess (a saturated solution of potassium ferrocyanide trihydrate or a 5 per cent solution of that salt in saturated potassium nitrate). After thorough mixing, the liquid is brought to the mark with saturated potassium nitrate solution, and the flask is shaken vigorously for 2 min. Its contents are then poured into a 50-ml graduated centrifuge tube and centrifuged until the precipitate has fully settled. Finally the volume of the precipitate is recorded, and a 25-ml sample of the clear supernatant liquid is taken with a pipet and titrated with standard, approximately 0.1N NaOH, using phenol red as the indicator.

In the calculations the volume of the liquid is taken as the figure obtained by subtracting the volume of the wet precipitate from the rated capacity of the calibrated flask. This overcorrects slightly for the volume of the precipitate, but the error so caused is only a small fraction of that which would be introduced by failure to make any correction for the volume of liquid displaced.

When it is necessary to carry out the precipitation in a strongly acid solution, about 1.5N, for example, the liquid should be brought as near as practicable to complete saturation with potassium nitrate. This result is conveniently brought about by adding a little of the solid salt and prolonging the shaking. The volume of any crystals that remain undissolved simply increases the observed volume of the precipitate and hence causes no error. However, unduly high acidity can be avoided by taking a smaller sample for analysis, and this course is generally preferable.

(b) Procedure for Water Solutions.³³ The sample is precipitated with potassium ferrocyanide in the same manner and with the same precautions employed in the case of the ether solutions. The sample is then centrifuged, with the volume of the precipitate noted. A definite volume of the supernatant liquid is taken with a pipet and is titrated potentiometrically with standard 0.01N NaOH, using a pH

meter and laying special stress on the accuracy of the readings taken between pH 3.5 and 5. The curve is then extrapolated to allow for the aluminum content.

The curve to be extrapolated, drawn on coordinate paper thin enough for tracing, is superimposed on a carefully drawn graph of a normal nitric acid neutralization curve. Both curves must be drawn to the

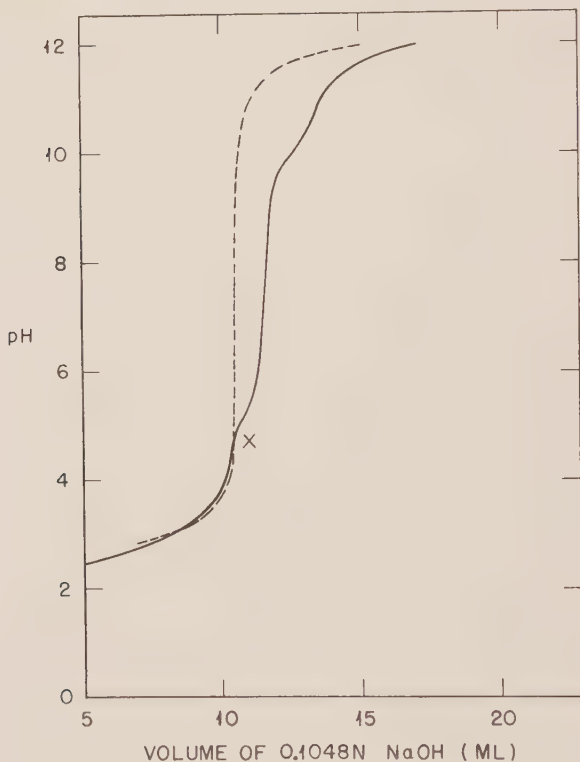


Fig. 3.1—Titration with NaOH of the HNO_3 liberated from uranyl nitrate.

same scale, and the two titrations should be carried out under similar conditions as to dilution. The two sheets are then adjusted so that horizontal lines of like pH coincide, while at the same time the point X (see Fig. 3.1), which marks the beginning of the aluminum break, lies exactly on the lower curve. The upper curve is then extrapolated from point X to a distance beyond the neutral point by tracing the course of the lower curve. The true end point of the titration, which will lie on the extrapolated portion, can then be read off.

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Chapter 4

SILICON

By K. J. Jensen and C. J. Rodden

Determinations of silicon were required in uranium ores and uranium metal. The determination of macro amounts of silicon as silica followed usual procedures given in standard texts.

The conventional molybdosilicic acid method was used for the colorimetric determination of silica. The carrier-distillation method was used extensively in the spectrographic analysis of uranium and its compounds and is described in Chap. 26 on "Spectrochemical Methods."

1. METHODS OF SOLUTION

Uranium and its compounds are readily dissolved in nitric acid. Ores and minerals are dissolved by conventional methods.^{1,2}

Aluminum-silicon alloys were disintegrated with an acid mixture (485 ml of water, 115 ml of sulfuric acid, 200 ml of hydrochloric acid, and 200 ml of nitric acid), heated until sulfur trioxide fumes appeared, cooled, and diluted with water; the residue was filtered off, ignited, and fused with sodium carbonate. The melt was dissolved in dilute sulfuric acid, and the silicon was determined in the usual manner. This method, although not tested critically, appeared to give reliable results because the aluminum and silicon values of the same sample consistently added up to 100 ± 0.5 per cent. However, for the analysis of an unknown aluminum-silicon alloy it is recommended that the sample be disintegrated with a sodium hydroxide solution because some silicon is lost as the hydride when certain types of aluminum-silicon alloys are treated with the acid mixture mentioned above.^{3,4}

The presence of fluorine in the sample that is to be analyzed is a disturbing factor because some silicon is usually lost as the tetrafluoride upon the usual treatment with acid. For such samples fusion

with a mixture of sodium carbonate and borax serves not only to separate the fluorine as a volatile boron trifluoride but also to convert any silicon or insoluble silicates to soluble silicates. A method developed for fluorspar⁵ has been applied⁶ to UF_4 . In this method the sample is dissolved in a 20 per cent perchloric acid solution, which has been saturated with boric acid at 50°C , and then heated to fuming.

Sodium peroxide fusion has been used^{7,8} to decompose UF_4 prior to a silicon determination.

2. METHODS OF SEPARATION

For most purposes the dehydration of silicic acid serves as a separation.⁹ If tin is present the silicic acid should be dehydrated with sulfuric or perchloric acid; lead can be separated from silica by using perchloric acid. Boron, if present, is usually carried down to some extent with the silica, and it must be separated to prevent volatilization as the trifluoride along with the silicon tetrafluoride. Refluxing the precipitate with a small amount of methyl alcohol that has been saturated with hydrogen chloride gas causes the boron to be volatilized as methyl borate.¹⁰

3. METHODS OF DETERMINATION

There is little choice of methods for the determination of silicon. For macro concentrations the gravimetric procedure gives accurate results. For micro concentrations the colorimetric method is simple, rapid, and accurate within a few per cent. Spectrographic methods that are fairly sensitive and that present no special problems are discussed in Chap. 26, "Spectrochemical Methods." Table 4.1 gives the range of the methods employed.

3.1 Gravimetric. The methods employed for the determination of silicon in uranium and its alloys, nickel, and beryllium, consisted of the classical methods of dehydration by hydrochloric, sulfuric, or perchloric acids. The silicic acid is removed by filtration, and after ignition it is volatilized with hydrofluoric acid.¹¹⁻¹⁶

(a) Determination of SiO_2 in Uranium Metal and Oxide. Procedure.¹⁷ Approximately 50 g of the clean metal is weighed and transferred to a Coors No. 4A porcelain casserole, 150 ml of HNO_3 is added, and the casserole is covered with a watch glass. The casserole and its contents are then placed on a steam bath, and the reaction is allowed to proceed until the metal is in solution. The underside of the cover glass is washed off, and the solution is removed from the steam bath and transferred to a hot plate covered with a thin sheet of asbestos.

The evaporation is continued until crystallization takes place. The casserole is rotated occasionally to facilitate crystallization on the sides of the dish and not on the bottom. When a solid mass of crystals has formed, it is removed from the hot plate and allowed to cool. The crystals are then treated with 90 ml of HNO_3 (1 to 1) and covered with

Table 4.1—Range of Methods for Silicon

Method	Range
Gravimetric	> 200 γ
Colorimetric	0.05–200 γ
Spectrographic:	
Carrier-distillation	3 ppm limit
Copper spark	0.01 γ limit

a watch glass, and the casserole and its contents are placed on the steam bath. The solution is stirred occasionally with a glass rod until the crystalline mass has dissolved and the solution appears clear. The solution is filtered through Whatman No. 42 11-cm filter paper containing a small amount of macerated paper pulp, and the filter paper is washed at least ten times with hot HNO_3 (1 to 99). The paper and residue are placed in a weighed platinum crucible, and the paper is burned off.

The filtrate is transferred back to the original casserole and again evaporated to crystals as previously. When the crystallization is complete, the sides of the casserole are heated with the flame of a bunsen burner until all the salts that adhere to the inside of the casserole turn a deep-red or dark-orange color. Most of the crystalline mass will fall to the bottom of the dish, and some of it will redissolve. The evaporation is continued to dryness, the asbestos is removed from the hot plate, and the casserole is heated until no more fumes are evolved. The casserole is removed from the hot plate and cooled, and the sample is treated with 90 ml of HCl (1 to 1). It is then covered with a watch glass, and the sample is redissolved as before. The insoluble material is filtered off on a Whatman No. 42 11-cm filter paper that contains a small amount of macerated paper pulp and is washed at least ten times with HCl (1 to 99).

The insoluble material is combined with the original insoluble material, and the paper is burned off. The contents are ignited for 15 to 20 min at 1000°C and then cooled and weighed as the insoluble residue. The ignited residue in the crucible is treated with 1 or 2 drops of water, 3 or 4 drops of H_2SO_4 , and 3 to 5 ml of HF (48 per cent). It

is then evaporated to dryness. This procedure is repeated, and the residue is ignited for 5 min at 1000°C and then weighed.

The difference between the weight of the total insoluble material and the insoluble residue after the HF treatment gives the weight of silicon dioxide.

(b) Determination of SiO_2 in UF_4 . Procedure.⁶ A 3-g sample is weighed into a 400-ml pyrex beaker, and to this are added 4 g of H_3BO_3 and 25 ml of HClO_4 . The beaker is covered with a watch glass and placed on a hot plate, and the sample is heated until it has dissolved; it is then fumed for about 10 min. (A blank and a control sample to which 10 mg of SiO_2 has been added are also run.) It is then cooled, diluted to 200 ml, and filtered, and the filter paper is washed 20 times with hot dilute HCl (1 to 99). (It is necessary to remove the HClO_4 completely.) The filter paper is burned off in a platinum crucible, and the residue is ignited, cooled, and weighed. To the residue are added 5 drops of H_2SO_4 and 1 to 2 ml of HF , after which it is evaporated to dryness, reignited, cooled, and weighed. The SiO_2 content is calculated from the loss in weight.

3.2 Colorimetric. The determination of silicon as the molybdenum blue complex¹⁸ has been employed for soluble silica.¹⁹⁻²¹

Silicates in dilute acid solution react with molybdate ion to form a complex molybdosilicic acid. This complex acid is extracted with organic solvents such as amyl²¹ or *n*-butyl alcohol²⁰ to form molybdenum blue, and the transmittancy of the solution is then measured at 800 μ .

The acidity of the solution is an important factor affecting the formation and extraction of the heteropoly acid. It has been found that molybdosilicic acid is not formed above an acidity of 0.9N. The optimum acidity for the formation and extraction of the complex is 0.3N. Other workers used a modification recommended by Schwartz,²² who employed oxalic acid to decrease the phosphate interference. In their method vanadate, tungstate, and arsenate do not interfere. Glass containers, which are ordinarily used for the storage of solutions, are to be avoided owing to the possibility of silicate contamination. Wax-lined bottles or plastic containers should be used for all except the amyl alcohol-ethyl acetate solutions.

(a) Determination in the Presence of Phosphate. The following method has been used for the analysis of soluble salts of uranium in the presence of phosphate.

Procedure.²¹ A 1-g sample is dissolved in 20 ml of water. To this are added 5 ml of 0.5N HCl and 5 ml of 10 per cent ammonium molybdate solution, and the solution is allowed to stand for 5 min. Now 3 ml of a 10 per cent solution of oxalic acid is added, and the solution is

stirred until the precipitate formed has dissolved. The solution is transferred to a separatory funnel, 10 ml of HCl (1 to 2) is added, and the solution is extracted with several 2-ml portions of amyl alcohol-ethyl acetate.¹⁹ The combined extracts are washed with 5 ml of 0.5N HCl and transferred to a dry 25-ml stoppered graduated cylinder together with another 5-ml portion used for washing out the separating funnel. The volume is made up to 20 ml, 4 drops of stannous chloride solution (50 g of SnCl_2 + 50 ml of HCl diluted with 50 ml of H_2O) is added, and the solution is mixed and allowed to stand for 5 min. The absorbency is measured in a Spekker absorptiometer against a water blank using a 1-cm cell and red filters. A blank is carried out on 2 ml of NH_4OH and neutralized with HCl under the same conditions as used in the determination.

(b) Determination in the Absence of Phosphate (Range 0.5 to 14 γ). In order to avoid contact with ground glass the apparatus shown in Fig. 4.1 has been employed.

The bulb should have a volume of at least 25 ml, and the tip should be long enough to reach the bottom of a 25-ml beaker. The solutions are drawn into the separatory funnel and are mixed by the use of suction. After the solutions are mixed, they are removed from the chamber by means of pressure. A waterhead of about 4 ft serves as a convenient source, or a syringe may be used. A water trap is placed between the waterhead and the funnel. A screw clamp is placed on the rubber tubing connection as another aid in controlling the pressure. With a little practice clean separations can be made. The distilled water used is obtained from an all-metal still and stored in wax-lined bottles.

Procedure.²⁰ A solution of the sample containing 0.5 to 14 γ of silicon as soluble silicate is placed in a 25-ml waxed beaker. This is carefully drawn into the separatory funnel by suction. Following this, 2 ml of 6.25 per cent ammonium molybdate, 3 ml of 1N H_2SO_4 , and enough distilled water to make 10 ml are added, one after the other. (The ammonium molybdate, H_2SO_4 , and water are each poured into and drawn from the beaker that contained the sample, thus ensuring a quantitative transfer of the sample.) The final solution is permitted to stand for 5 min, and then 10 ml of *n*-butyl alcohol is drawn into the funnel from a 25-ml beaker (not waxed). Extraction of the water layer is then performed by regulating the suction so that complete mixing is effected without causing the liquid to spatter from the upper portions of the funnel. Extraction is continued for 2 min. After the two phases have been allowed to separate, the water layer is discarded by applying pressure. The butyl alcohol is washed twice with 5-ml portions of 0.3N H_2SO_4 , and the washings are discarded.

Then 3 ml of 0.6 per cent stannous chloride solution (40 per cent SnCl_2 in HCl , diluted) is introduced from a waxed beaker, and the two layers are again thoroughly agitated with the aid of suction for 15 to 30 sec. The two phases are allowed to settle for a few minutes. The water layer is discarded, and the blue butyl alcohol layer is transferred to a 10-ml volumetric flask. The funnel is rinsed with a little 95 per cent ethyl alcohol by means of suction, and the liquid is then removed

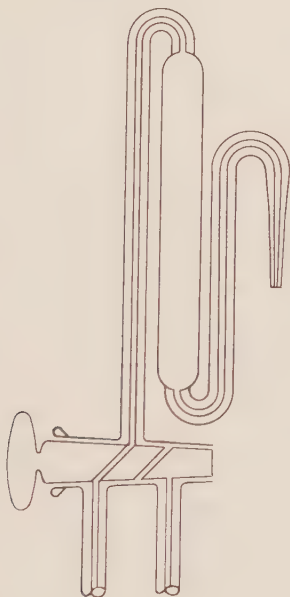


Fig. 4.1—Separatory funnel used in spectrophotometric method of determining silica.

by pressure and combined with the butyl alcohol. The solution is then diluted to volume with butyl alcohol and transferred to a 1-cm absorption cell, and the transmittancy is measured at $800\ \mu$, using a Beckman spectrophotometer, against butyl alcohol. A blank on the reagents is carried through the same procedure as the sample. The weight of silicon is obtained from a previously prepared calibration curve.

(c) Determination in the Absence of Phosphate (Range 0.02 to $2.5\ \gamma$). By utilizing proportionately smaller volumes of reagents and by measuring the transmittancy of the silicon complex in a final volume of 1 ml, West et al.¹⁹ have increased the sensitivity of the above pro-

cedure by a factor of 10. In this procedure the extractor used is similar to that shown in Fig. 4.1, but it has a bulb volume of about 10 ml.

The redistilled water used for the preparation of all reagents, as well as that used in washings, should not touch any glass surface after being taken from a metal still.

All solutions except *n*-butyl and ethyl alcohol are stored in paraffin-lined bottles with plastic caps or with paraffin-coated corks. Dust caps are provided to lessen silica-dust contamination.

Transfer of liquids to the funnel through the tip is made by use of moderate suction from an aspirator pump. Each reagent is drawn in from a small beaker reserved for that particular reagent only. Removal of liquids from the funnel is accomplished by slight air pressure through the stopcock.

Since the degree of acidity controls the formation and extractability of the molybdosilicic acid, the sample must be neither excessively acidic nor basic. The optimum mineral acid normality for the process has been found to be 0.3N,²⁰ and if possible the acid content of the sample should approximate this value.

Procedure.¹⁹ The sample, which has an acid content of about 0.3N and contains 0.02 to 2.5 γ of silicon in a volume not greater than 0.45 ml, is transferred to the separatory funnel. To this are added successively 0.25 ml of 6.25 per cent ammonium molybdate [$6.25 \text{ g } (\text{NH}_4)_6\text{MoO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 100 ml of water] and 0.30 ml of 1N H_2SO_4 . The solution is mixed by use of suction and is allowed to stand for 5 min. One milliliter of *n*-butyl alcohol is added, and the mixture is agitated by suction for 2 min. When the two layers have separated, the water layer is removed and discarded. The alcohol phase is washed for about 30 sec with two separate 0.8-ml portions of 0.3N sulfuric acid. A volume of 1.5 ml of 0.2 per cent SnCl_2 (40 per cent SnCl_2 in HCl , diluted) is added, and the two phases are mixed by suction for 30 sec. The aqueous layer is removed and discarded, and the alcohol is transferred to a 1-ml volumetric flask. The funnel is rinsed with 0.2 ml of ethyl alcohol. The rinsings are added to the volumetric flask, and the solution is diluted to 1 ml; it is then mixed and transferred to a 4-ml absorption cell having a 1-cm light path.

The transmittancy of the solution is measured against water, using a Beckman spectrophotometer at 800μ . The cell is placed on a brass block (Fig. 24.3), which raises it so that the major portion of the light passes through the bottom of the cell.

The amount of silicon is determined from a previously prepared calibration curve.

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Chapter 5

FLUORINE AND FLUOROCARBONS

1. FLUORINE

By G. W. Busch, R. C. Carter, and F. E. McKenna

Fluorine is the most powerful oxidizing agent known. It reacts directly with all the elements except nitrogen and the noble gases. Therefore, analysis of gaseous mixtures containing fluorine is difficult because of its reaction with the container and with any confining liquids. It apparently forms compounds only in which it is univalent. Many volatile fluorine compounds are known.

Fluorine is almost always determined as a fluoride. Relatively few satisfactory methods exist for the analysis of gaseous fluorine.

The fluorides of lithium, the alkaline earths, thorium, and the rare-earth metals are only slightly soluble in water. Because many fluorine compounds are relatively insoluble and determinations of fluorine are subject to many interferences, a preliminary separation is of great importance in virtually all determinations.

1.1 Methods of Solution. A great many fluorine compounds can be decomposed by treatment with sulfuric acid and powdered silica or by treatment with perchloric acid. Some refractory materials and siliceous ores, however, are not decomposed by such treatment. The fluosilicic acid that is formed can then be distilled and determined as described in Sec. 1.3. An apparatus for the simultaneous decomposition of the sample and distillation of fluosilicic acid is shown in Fig. 5.1. The fluosilicic acid distillation method may be used for calcium fluoride powder, if perchloric acid is substituted for sulfuric acid.¹

Fusion with sodium carbonate to form soluble sodium fluoride is widely used as a decomposition method.^{2,3} Decomposition of fluor-spar is accomplished by fusion with potassium carbonate and potassium nitrate in a platinum crucible.²

Uranium tetrafluoride has been brought into solution by mixtures of boric and hydrochloric acids,^{4,5} aluminum chloride and hydrochloric acid,⁶ boric and sulfuric acids,⁷ and hydrochloric and nitric acids.⁸

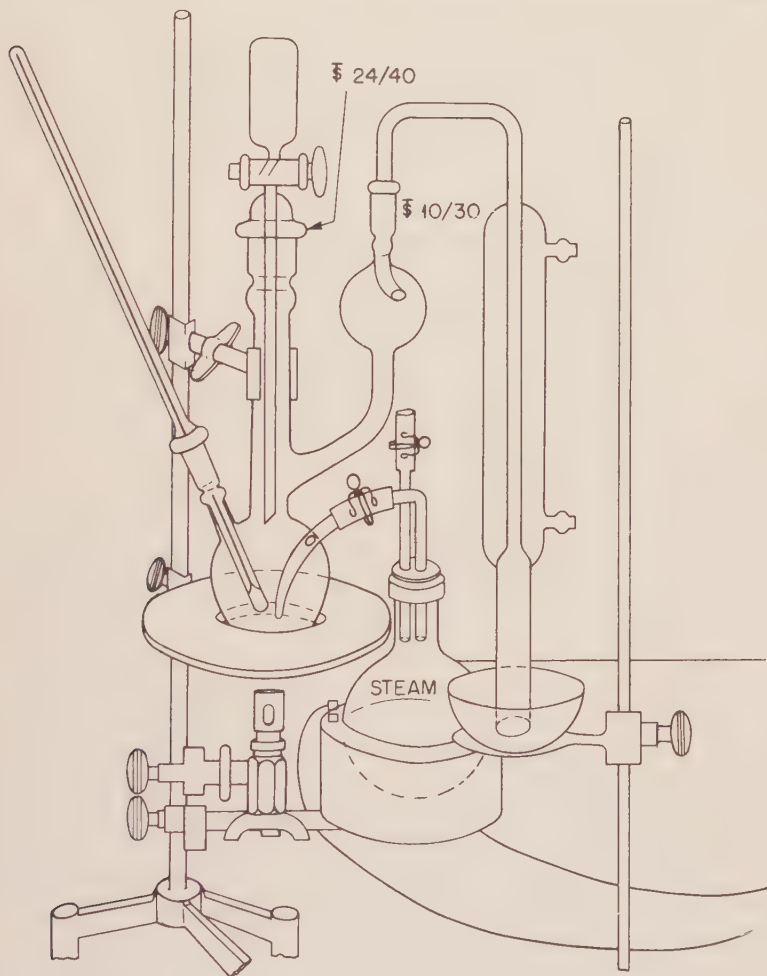


Fig. 5.1—Apparatus for simultaneous sample decomposition and distillation of fluorine.

The quantitative solution of fluorine compounds which tend to decompose in air, such as uranium hexafluoride, has been effected by solution in dilute nitric acid in a pressure bottle. The fluoride may then be distilled as fluosilicic acid. The solution of fluorine-contain-

ing compounds is quantitative when this method is used, while fusion of similar compounds with sodium hydroxide was found to give low fluoride recovery.⁹

In general, solvent extraction methods are not applicable. In certain cases, however, it is possible to extract films of fluoride from metal surfaces without disturbing the unattacked substrate and without changing the valence of the constituents to be determined. Nickel, iron, copper, and uranium fluorides have been extracted by using either a methanol or an ice-water extraction. The solubility of uranyl fluoride in warm methanol has been used for its determination in uranium tetrafluoride.¹⁰

The quantitative decomposition of organic fluorine compounds is particularly difficult to accomplish. Quantitative decomposition of fluorocarbons by the use of a Parr bomb charged with potassium nitrate, sugar, and sodium peroxide has been reported.^{11,12} A more satisfactory method is the fusion of the fluorine-containing compound with metallic potassium or sodium in specially designed bombs.¹³⁻¹⁵ A special combustion train has been developed for the analysis of organic compounds, in which all hydrogen atoms have been replaced by fluorine or other halogens.¹⁶

1.2 Methods of Separation. Fluorine is generally separated as fluosilicic acid² from sulfuric or perchloric¹⁷ acid solution by using an apparatus similar to that shown in Fig. 5.1. Precipitation of fluorides as calcium fluoride is not an ideal separation procedure because of the solubility of this compound. Aluminum interferes because of the formation of a stable complex, $(\text{AlF}_6)^{-3}$, which does not decompose at 135 to 150°C in acid. The procedure is essentially the one given by Willard and Winters.¹⁷ It is described in detail below.

Watters et al.¹⁸ designed a special platinum cell in which fluorine is separated as hydrogen fluoride. The hydrogen fluoride is volatilized in a stream of nitrogen from a 50 per cent solution of sulfuric acid kept at 125°C. The cell, with its brass heating block, is shown in Fig. 5.2. Separation and recovery of 0.05- to 0.5-γ amounts of fluorine have been performed by the distillation of hydrogen fluoride from a platinum retort.^{18,19}

Pure gold solder was used in fabricating the cell. The stopper on the inlet of the cell was sealed by rotation, with vaseline used as a lubricant. The inlet of the cell is rather large in order to permit the introduction of solid samples and reagents directly to the bottom of the cell. When in use, two cells and a thermometer are placed in holes in a brass heating block, which is heated by a nichrome wire wound over asbestos and controlled by a Variac. A cell that is held together by stainless-steel rings is shown in Fig. 5.3.

Procedure.¹⁸ The best recoveries were obtained when the sample in 0.5 ml of 50 per cent H_2SO_4 was kept at $125 \pm 2^\circ\text{C}$ for 40 to 50 min distillation time. The nitrogen, at a rate of 100 to 150 bubbles per minute, was washed by passing through successive wash towers filled with sulfuric acid, dilute sodium hydroxide, and finally water warmed

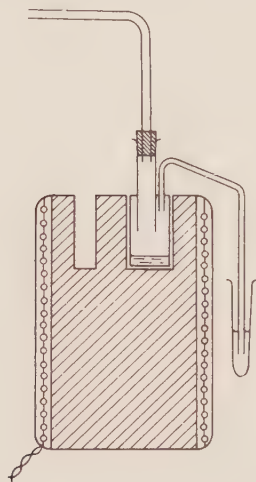


Fig. 5.2—Nitrogen-swept platinum cell and heating block. Dimensions of platinum cell: cell proper, 1.0 cm inside diameter, 2.3 cm height; neck of cell, 4.5 mm inside diameter, 3 cm total height; inlet and outlet tubes, 2 mm inside diameter.

to 60°C . After the cell is filled, it is placed in the block, which has previously been adjusted to the desired temperature. The outlet is inserted to the bottom of a 3-ml centrifuge cone containing 1 ml of 0.0003N NaOH.

1.3 Methods of Determination. Fluorine may be determined gravimetrically as lead chlorofluoride^{2,20,21} or as calcium fluoride;²² titrimetrically by titration with thorium nitrate by using sodium alizarinsulfonate as the indicator (see references 9, 13, 15, 17, 23-34); colorimetrically by using peroxytitanic acid;^{35-37,76,77} fluorometrically by using morin;^{38-42,116} or potentiometrically by using a ferrous-ferric concentration cell (see references 18, 21, 42-44).

No appreciable difference is found in the accuracy obtainable by using the two gravimetric methods.⁴⁵ The calcium fluoride method is tedious and requires strict attention to details. The lead chlorofluoride method is much more rapid and convenient, especially in the range of 0.01 to 0.1 g of fluorine. Greater accuracy is obtained when the lead chlorofluoride precipitate is dissolved and the chloride is

determined by Volhard's method; in this way errors due to coprecipitation are eliminated.

The thorium nitrate titrimetric method, with sodium alizarin-sulfonate as the indicator, is quite widely used. By varying the concentration of thorium nitrate a wide range of fluoride concentration can be determined. The method is both rapid and accurate.

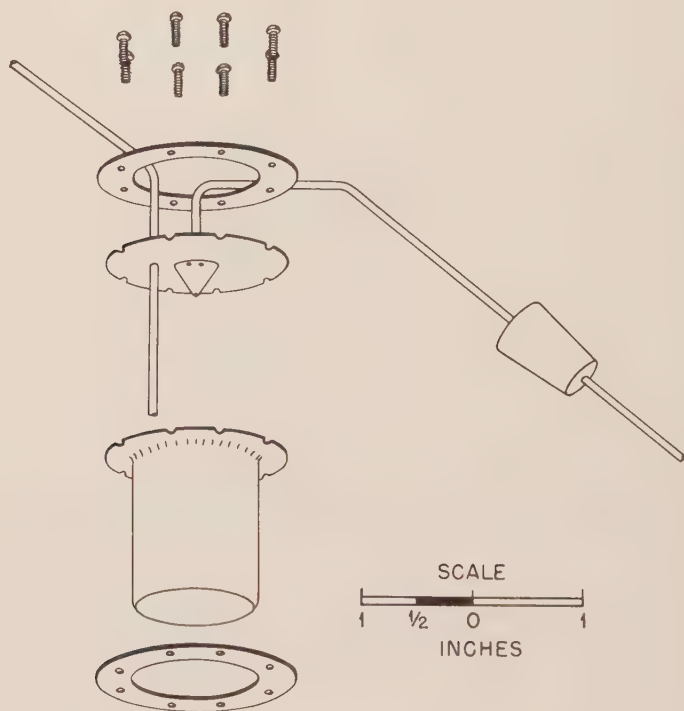


Fig. 5.3—Platinum still for hydrogen fluoride evolution.

The accuracy of the colorimetric method using peroxytitanic acid is not so great as the titrimetric method, nor is it applicable in as many situations, but it is quite sensitive. Fluorides can be determined colorimetrically by their bleaching action on solutions of ferric ion and orthophenolic acids, such as salicylic or cresotinic acids.⁴⁷ The quenching action of fluoride ion on the aluminum-morin fluorescence is very useful for small amounts of fluoride.

Elementary fluorine and gaseous mixtures of fluorine and other fluorine-containing compounds have been analyzed by a number of

methods. If no other reactive gases are present, fluorine can be quantitatively absorbed by mercury.^{47,48} The fluorine can be passed through sodium iodide,^{49,50} sodium bromide,⁵¹⁻⁵⁴ or sodium chloride⁵⁵ to liberate iodine, bromine, or chlorine, respectively. The liberated halogens are determined iodometrically, or the bromine is determined colorimetrically.⁵⁴

Gases containing potentially ionizable fluorine can be analyzed colorimetrically by use of the color change produced when zirconium azophenylarsonic acid is exposed to fluorine compounds.⁵⁶

Hydrogen fluoride can be determined by its vapor pressure after freezing out and separating other gases.⁵⁷

The activity of liver esterase is inhibited in proportion to the fluoride concentration and may be used for its determination.⁵⁸

The ranges of the various procedures used are summarized in Table 5.1.

(a) Gasometric Methods. Most inorganic fluorine-containing gases and their hydrolysis products are corrosive. Many metals and organic compounds will ignite when brought into contact with fluorine. Fluorine is toxic and should not be inhaled, even in exceedingly small concentrations. Adequate ventilation must therefore be provided for the operator.

When gas samples at pressures greater than atmospheric are being handled, a barricade of 1/4-in. cold-rolled steel with a course of brick forms a satisfactory protective barrier. Fluorine fires can be caused by moist or oily packing in the valves. Clean, dry polytetrafluoroethylene or other fluorocarbon materials can be used as a satisfactory packing material in the valves.

Valves should be only slightly "cracked." A sudden surge of fluorine into a reagent tube may result in a reaction sufficiently vigorous to raise the temperature to such a point that the metal of the inlet line or of the reaction tube may be burned through because of the heat developed.

Before exposure to fluorine the entire system must be thoroughly dried and degreased. In general, the greatest rises in temperature are experienced during the first exposure of the system to the fluorine. All connections should be silver-soldered or made by flare connections.

Methods for handling fluorine are more extensively discussed in Volume 6, Division II of the National Nuclear Energy Series.

(1) Mercury Absorption Method.⁴⁷ A measured volume of a gas mixture containing fluorine is brought into contact with mercury. Fluorine is quantitatively absorbed by the mercury, and the residual gases are analyzed for oxygen and inert gas by the Orsat method.

Fluorine purity may be determined within 0.5 per cent over a range of 0.5 to 100 per cent fluorine.

The gas is first drawn through a potassium fluoride or liquid-oxygen trap to remove hydrogen fluoride. It is then allowed to flow

Table 5.1—Methods of Determination

Method	Range or limit	Accuracy, %
Gasometric:		
Mercury absorption	0–100%	0.5
Manometric, for HF in F ₂	0–1%	0.1
Gravimetric:		
Lead chlorofluoride	0.01–0.10 g	
Calcium fluoride	0.01–0.10 g	
Volumetric:		
Lead chlorofluoride (Volhard)	0.01–0.10 g	
Thorium nitrate	0.05–12 γ	15–2.5
Potentiometric Fe ⁺² –Fe ⁺³ electrode	0.02–2 γ per ml	10
Iodide-acidimetric		
Sodium fluoride–sodium chloride		
Hydrolytic, sodium hydroxide		
Colorimetric:		
Peroxytitanic acid	0.1–2.5 mg	
Zirconium <i>p</i> -dimethylamino-azophenylarsonate	1–500 ppm	10
Ferric-salicylic acid complex	0.1–140 γ per ml	
Bromine displacement	0–20 vol. %	2
Congo red, visual		
Fluorometric:		
Aluminum–morin	0.005–0.50 γ per ml	20
Polarographic:		
Catalytic nitrate wave	1 γ per ml	7
Enzymatic:		
Hog-liver esterase	0–10 ppm	5
Spectrographic		

through the previously evacuated sampling bulb with an exit in a hood. Stopcocks should be lubricated with a completely fluorinated oil or grease.

The apparatus is constructed of pyrex and is shown in Fig. 5.4.

After the bulb has been filled to a known pressure, the mercury from the leveling bulb is exposed to the gas sample. The surface of the mercury will become coated with a fluoride layer. The mercury

should be agitated to expose fresh mercury surface until all the fluorine has reacted.

After the decrease in volume due to the absorption of fluorine has been determined, residual gases may be determined by the usual

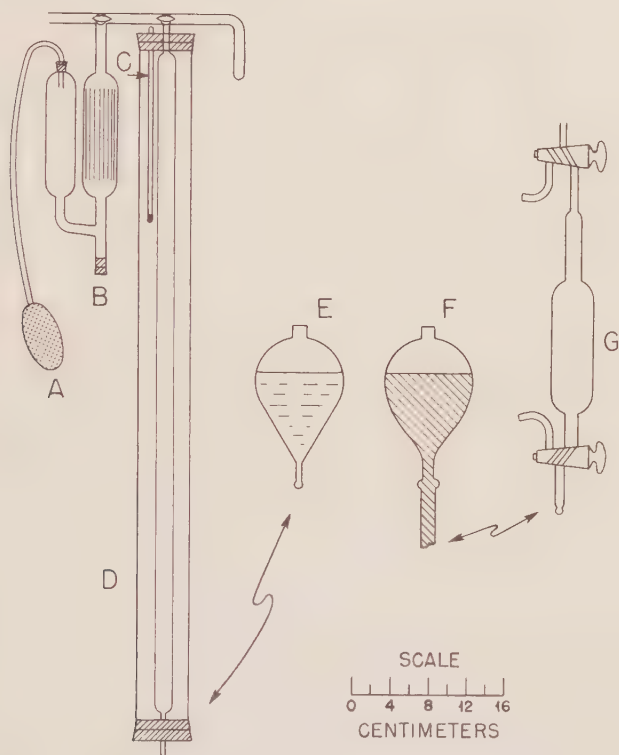


Fig. 5.4 — Gas-analysis apparatus. A, gas expansion bag; B, gas pipet; C, thermometer; D, gas buret; E, water-leveling bulb; F, mercury-leveling bulb; G, sampling tube.

Orsat procedures. Alternatively, the decrease in pressure may be measured.⁴⁸

(2) Manometric Method for Hydrogen Fluoride in Fluorine.⁵⁷ A known volume of fluorine is condensed at 80°K and then evaporated off, leaving solid hydrogen fluoride. The hydrogen fluoride is then allowed to vaporize into a closed system of known volume. After the attainment of temperature equilibrium, the pressure of the hydrogen fluoride is determined with a Moore Nullmatic bellows manometer.

The accuracy of the method is equivalent to the accuracy of measurement of the pressures, volumes, and temperatures. However, the adsorption of hydrogen fluoride by the metal parts of the system, the possible presence of condensable silicon fluorides, and uncertainty as to the molecular weight of hydrogen fluoride make additional precision unnecessary. The adsorption error is probably of the order of 0.1 per cent. This method has been used for fluorine samples containing hydrogen fluoride in the range of 1 mole %.

(b) Gravimetric Methods. (1) Determination as Lead Chlorofluoride.² Fluorine is precipitated as lead chlorofluoride, and the precipitate is weighed. This method has been used extensively in the analysis of various materials and specifically for uranium fluorides.²⁰ The presence of 0.5 mg of aluminum or iron, 50 mg of boron, 0.5 g of ammonium ion, or 10 g of sodium or potassium salts seriously interferes with accurate determination. Aluminum and iron may be removed by an ammonium carbonate precipitation. The best results are obtained when the fluoride content is about 100 mg. In the range of 10 to 20 mg the method yields erratic results, which tend to be low. Lead chlorofluoride is soluble in water to the extent of 0.325 g per liter at 25°C. In order to prevent some of the loss of precipitate, it is washed with a cold saturated solution of lead chlorofluoride. Beans et al.²⁰ used the gravimetric method, since almost the same results were obtained as with the volumetric method.

(2) Fluorine in UF_6 .²⁰ The tube containing the weighed sample of UF_6 is broken under 300 ml of water containing 10 ml of 6M NaOH. When the sample is completely decomposed, 3 drops of bromphenol blue are added to the solution, which is then acidified with 6M acetic acid and made up to 500 ml. Aliquots of this solution containing approximately 100 mg of fluoride are taken for the determination.

Three milliliters of 10 per cent NaCl solution is added, and the solution is diluted to 250 ml. The solution is made just alkaline with dilute NaOH. Two milliliters of HCl (1 to 1) and then 5 g of lead nitrate are added, and the mixture is heated until the salt is in solution. Five grams of sodium acetate is added, and the mixture is stirred and digested on a hot plate for 30 min. After standing overnight, the precipitate is filtered in a porous-bottom crucible and washed with a saturated solution of lead chlorofluoride and, finally, once with water. It is then dried at 135°C and weighed. If it is not possible to run the determination on aliquots containing approximately 100 mg of fluoride, the same relative concentration should be maintained by adjusting the volume and quantity of the reagents.

(3) Determination as Calcium Fluoride. The method that has been used is adequately described in standard works.²²

(c) Volumetric Methods. (1) Lead Chlorofluoride Method. While the fluorine may be weighed as lead chlorofluoride, errors due to coprecipitation are eliminated by dissolving the precipitate in dilute nitric acid and titrating the chloride by Volhard's method. This method was used by Hunt and Isom¹⁴ in the analysis of fluorocarbons.

(2) Thorium Nitrate Method (see references 9, 13, 15, 17, 23-32, 34, 38). Fluorine is separated as fluosilicic acid by distillation at 135°C by using the apparatus shown in Fig. 5.1. The distillate is titrated with thorium nitrate. Stoichiometric relations do not hold for this titration. Therefore the true normality of the thorium nitrate solution cannot be used to calculate the amount of fluoride present, and a standardization curve must be prepared. The thorium nitrate solution is standardized against solutions prepared from recrystallized and dried sodium fluoride. Substances such as aluminum, boric acid, and inert silicates interfere with the separation by retarding volatilization. Any ion that forms a precipitate or nondissociated salt with fluorine or thorium interferes.

The distillation flask should be thoroughly cleaned at frequent intervals to prevent the formation of an inert silicate film, which might pick up small amounts of fluoride by formation of the insoluble and nonvolatile silicon oxyfluoride.

Sodium alizarinsulfonate is used as the indicator for the thorium nitrate titration. The end point is the formation of a pink lake. Two modifications have been reported to obtain a sharper end point. In one method the distillate is concentrated to one-tenth of its volume after making the solution just basic to phenolphthalein. Then an equal volume of 95 per cent ethanol is added, and the sample is titrated. The ethanol is added to hasten complete precipitation of the thorium fluoride, permitting a sharper indication of the formation of the pink thorium lake.^{17, 59-62} An apparently contradictory method is based on the action of a starch solution as a protective colloid to inhibit the precipitation of thorium fluoride.^{26, 63}

A useful and stable end-point color standard has been found to be 2.33 g of cobaltous nitrate hexahydrate and 0.0279 g of potassium chromate dissolved in water and diluted to 1 liter.²³

A range of about 0.05 γ to 16 mg of fluoride may be obtained by varying the thorium nitrate concentration. The accuracy of the determination varies from ± 15 to ± 2.5 per cent in the 1- to 12- γ range to ± 0.1 to ± 0.2 per cent in the analysis of samples containing 1 to 16 mg of fluoride.

Chromazurol S (Solochrome Blue), the sodium salt of sulfodichlorohydroxydimethylfuchsondicarboxylic acid, has been satisfactorily substituted for alizarin as the indicator in samples containing 20 to

100 γ of fluoride. The end point of the titration is the change from the pink dye to the blue dye of the thorium lake. The end-point color can be matched with a mixture of $\text{Co}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ solutions, which may then be used as a permanent standard.⁶⁴ Other attempts to use Solochrome Blue dye as an indicator instead of sodium alizarin-sulfonate in the fluoride titration have shown that no definite end point can be detected when the fluoride ion content is greater than 1 mg. The end point is recognized more easily than the one obtained with sodium alizarinsulfonate in the 20- to 100- γ fluoride range. There is, however, a variance of about 0.2 ml of titrant in attempting to duplicate the Solochrome Blue end point.⁶⁵

Aluminum interferes in the ordinary fluorine separation and analyses because it forms the extremely stable complex $(\text{AlF}_6)^{-3}$, which is not decomposed in an acid solution at 135°C.

Aluminum has been separated by precipitation with oxine.⁶⁶ The fluoride remained quantitatively in solution during the precipitation of the aluminum. An ethanolic solution of oxine was used rather than the usual acetic acid solution, because acetic acid distills with the fluosilicic acid. An excess of oxine must be used to prevent the precipitation of aluminum hydroxide, which occludes a considerable amount of fluoride. If much calcium is present, "bumping" occurs during the distillation from sulfuric acid owing to the formation of a sludge of calcium sulfate. If the oxine is first removed by fusion with sodium carbonate and is then fused in an oxidizing matrix such as sodium peroxide, it is possible to distil from perchloric acid and thus prevent the bumping.

Procedure: F in UF_4 .³² One gram of UF_4 is transferred to a dry all-glass distillation flask (see Fig. 5.1). A 0.2-g sample of powdered silica is added, and the flask is connected with the condenser and the steam-generating flask. A 600-ml beaker containing 30 ml of water, 5 drops of phenolphthalein indicator, and 10 or 12 pellets of NaOH are placed under the condenser so that the condenser tip is immersed in the NaOH solution. Thirty milliliters of 72 per cent HClO_4 is added to the distillation flask through the funnel, and the stopcock is closed.

The burners under the two flasks are lighted and adjusted so that while the temperature in the distillation flask rises to 145 to 150°C, the nearly boiling water in the steam generator (about three-fourths full) is just beginning to produce steam. The temperature of the generating flask is regulated to give the required amount of steam, and the flame under the distilling flask is adjusted to hold the temperature between 140 and 150°C. The heating is continued in this range until 425 ml of distillate has been collected in the 600-ml beaker. If

the procedure is carried out properly, the distillate should remain cold. If the distillate becomes acid, one or two pellets of NaOH are added. The distillate is transferred to a 500-ml volumetric flask and diluted to 500 ml. A 50-ml aliquot is put in a 150-ml beaker, and 5 drops of sodium alizarinsulfonate indicator (0.1 g of reagent in 200 ml of H_2O) are added. Then HCl (1 to 250) is added dropwise until the pink color is just discharged. Next, 5 ml of buffer solution (9.448 g of monochloroacetic acid and 2 g of NaOH in 100 ml of H_2O) is added, and the solution is titrated with 0.05N $\text{Th}(\text{NO}_3)_4$ solution to a permanent pink. At least two aliquots should be titrated for each determination.

(3) Potentiometric Method.²¹ The change in the electromotive force of an Fe^{++} to Fe^{+3} electrode upon the addition of fluoride may be measured potentiometrically. The concentration-cell method of Low and Pryde⁴⁴ was used for the determination of small amounts of fluorine (see references 21, 42, 43, 67, 68). Preliminary work had indicated that an analysis of 1 to 10 γ of fluorine in 5 ml of solution was feasible.⁴³ Refinement of this method made possible a sensitivity of 0.001 γ of fluorine in a volume of 10 to 20 μ liters, containing as little as 0.01 γ of fluoride.⁴² It was found necessary to use gold electrodes⁴² instead of the platinum electrodes recommended by Low and Pryde.⁴⁴ The electromotive force of a given solution cannot be reproduced more accurately than within a few millivolts. However, the change in electromotive force can be reproduced within 0.2 mv except in extremely large concentrations of fluoride (0.01M to 0.03M). If the hydrogen-ion concentration is between 0.004N and 0.03N, the electromotive force is not affected, but in concentrations greater than 0.03N the sensitivity drops rapidly. The time required for the cell to attain equilibrium is also affected by the hydrogen-ion concentration. The cell used at one installation⁴² consisted of 1 drop of ferrous-ferric solution suspended between a small gold coil electrode and a fine glass capillary. The capillary was filled with potassium chloride and agar; it led to a calomel electrode. The drop was kept in an atmosphere saturated with water to prevent evaporation. In order not to change the electromotive force of this small cell a resistance of 10^7 ohms was placed in series with the cell. The galvanometer current used in balancing the cell was amplified by the system of Du Bridge and Brown.⁶⁹

Fluoride was titrated potentiometrically⁶⁷ by using a glass electrode to adjust the pH. The pH of the alkali fluoride sample is first adjusted with an acid or base to about 7. The solution is then titrated with 0.01N thorium nitrate until the pH reaches about 4. The end point is found by graphically locating the inflection point on the pH

volume curve or by observing the volume of titrating agent that corresponds to the maximum pH change per unit volume of titrant added.

(4) Iodide-Acidimetric Method.⁴⁹ A gas sample is drawn into an evacuated glass bulb of 100 to 1,000 ml capacity to an absolute pressure of 0.1 to 0.2 atm. If the glass is clean and dry, the pyrex is not attacked by the low-pressure gas to a great extent. The adsorption problem is more serious, but if the sampling time is less than 15 sec, pressure equilibrium can be achieved with a minimum of adsorption.

An excess of potassium iodide solution is drawn into the sample bulb. Oxidation of the iodide is substantially complete after shaking for 1 min. The liberated iodine is titrated with standard thiosulfate by using starch as the indicator. More accurate results are obtained by first drawing in 20 to 30 ml of perfluorodimethylcyclohexane. The fluorocarbon may facilitate the complete reaction of the fluorine with the potassium iodide rather than the competing reactions with water, which use up fluorine.

A known excess of standard sodium hydroxide is now added, and the solution is back-titrated with standard hydrochloric acid to a phenolphthalein end point. Direct titration of the hydrofluoric acid with an alkali led to an indefinite end point, which quickly faded.

This method has been used for HF-F₂ mixtures containing less than 20 per cent of each constituent in the presence of inert gases, with the total pressure of the gas mixture at less than 1 atm. Analysis of gas mixtures at pressures greater than 1 atm by bubbling gas through an absorbing solution gives results that are low in fluorine and high in hydrogen fluoride. This condition would seem to indicate the loss of fluorine by the reaction



or by a similar acid-producing reaction.

(5) Sodium Fluoride-Sodium Chloride Method.⁵⁵ Any hydrogen fluoride contained in the fluorine is quantitatively adsorbed by sodium fluoride. The NaF, preferably in the form of pellets, should contain less than 3 per cent sodium fluosilicate. (These pellets are heated to 375 to 400°C and are swept with dry nitrogen until the hydrogen fluoride content of the effluent gas is less than 0.05 vol. %. The NaF is then exposed to fluorine for 2 hr at 100 to 150°C in order to remove organic matter as volatile fluorocarbons. Any HF now adsorbed on the NaF is removed by another heating in dry nitrogen at 400°C. After these treatments the pellets should contain less than 0.02 per cent hydrogen fluoride.) After the NaF has adsorbed the HF from a

fluorine sample, the pellets are macerated in ice water. The resultant solution is titrated at about 5°C with silicate-free sodium hydroxide to a phenolphthalein end point. A blank must be run on the NaF pellets.

After the hydrogen fluoride is removed, the fluorine is passed over sodium chloride. The chlorine is liberated and absorbed in a 2N sodium hydroxide solution. The resultant hypochlorite liberates iodine from iodide, and the iodine is titrated with a standard thiosulfate solution.

Any gas that is not absorbed by the sodium hydroxide may be analyzed for oxygen and inert gases in an Orsat apparatus.

The error in the hydrogen fluoride determination is less than 0.15 per cent.

A similar method⁷⁰ has used calcium chloride, dried at 180 to 200°C for 16 hr, instead of sodium chloride.

(6) Hydrolytic Method. Uranium, thorium, and other heavy-metal fluorides will react with superheated steam to form the oxide of the metal and hydrogen fluoride.^{71,72} Superheated steam is passed over the sample at 900°C in a platinum tube, and the hydrogen fluoride formed is determined titrimetrically with sodium hydroxide by using phenolphthalein as the indicator.⁷² The distillate is collected in a platinum or paraffin-lined dish after passing through a platinum condenser. The fluorides of the alkali and alkaline-earth metals hydrolyze very slowly; hence, low results are obtained for these compounds. Beryllium fluoride has been analyzed satisfactorily by this method.⁷³ Small amounts of fluoride in heavy-metal samples can be determined by this method.

The method may be used for the determination of both hydrolyzed and unhydrolyzed fluoride.⁷⁴ The hydrolyzed fluoride can be determined in the distillate. The unhydrolyzed fluoride can be distilled, as described in Sec. 1.3c(2), from the oxide residue resulting from the reaction of the steam with the metal sample.

Urine samples are ashed with calcium oxide in a nickel crucible. The fluoride is removed from the urine ash by distillation from a sulfuric or perchloric acid solution.^{34,75} Distillation of the chloride in the urine can be prevented by the addition of silver sulfate or silver perchlorate. If the distillate gives a positive test for chloride, it is rejected; or, if more than 0.2 milliequivalent of alkali is required to neutralize an aliquot of the distillate containing 15 to 30 γ of fluoride, the distillation is repeated. The distillate is then titrated with thorium nitrate solution by using sodium alizarinsulfonate as the indicator. A correction must be made for the fluoride content of the reagents, particularly the calcium oxide.

(d) Colorimetric Methods. Fluorides bleach the yellow color produced by the oxidation of tetravalent titanium to peroxytitanic acid.³⁷ The decrease in intensity may be measured colorimetrically. Fluorides also bleach alizarin lakes, but owing to the oxidizing action of chlorine, the reaction is of no value in the analysis of gaseous mixtures of fluorine and chlorine. An attempt was made to use the etching action of hydrogen fluoride to break fine glass filaments. This test was partly successful, but the necessary manipulations were too delicate. Manganous chloride tetrahydrate was found to change in color from a light rose to a dark brown when fluorine of concentration greater than 0.5 per cent was passed over it. Chlorine has no effect on the color of this salt.

(1) Peroxytitanic Acid Method. The test of Steiger⁷⁶ and Merwin⁷⁷ has been adapted to give a reliable quantitative determination. This test involves the bleaching action of fluoride ion on the color of peroxytitanic acid. If a large excess of hydrogen peroxide is used in the preparation of the peroxytitanic acid solution from titanyl sulfate, the chlorine will react with the peroxide and will not bleach the oxidized titanium compound. A large excess of peroxide has no effect on the bleaching action of the fluoride.

The method is accurate within about 10 per cent of the value of fluorine reported in the range of 0 to 5 per cent of fluorine in chlorine. None of the common gases interfere with this method as a qualitative test, but any volatile fluoride interferes with the quantitative determination.

The gas mixture can be absorbed in the peroxide-titanium solution in any type of gas absorption bottle. The solution is then transferred to the colorimeter cup of a photoelectric colorimeter.

Procedure.³⁶ A 2.5-g sample of titanyl sulfate or an equivalent amount of any other titanium salt is dissolved in 1 liter of sulfuric acid (1 to 6). If the solution is not clear it should be filtered. A 10-ml volume of the titanium solution, 3 ml of 30 per cent hydrogen peroxide, and 5 ml of 12N sulfuric acid are mixed, diluted to 100 ml, and shaken thoroughly. A 25- by 2-cm tube is filled three-fourths full of this solution, with the remainder saved for a standard. The gas sample is passed through the solution for 1 min at a rate of 50 ml per minute. The solution is then removed from the absorption cell, and a small amount is placed in a colorimeter cup. The solution is poured back and forth several times to remove dissolved gases. The transmittancies of the treated and untreated solutions are compared by using a green filter. The transmittancy maximum is at 525 m μ . The amount of fluorine is determined from a calibration curve.

The method has also been applied to the determination of fluoride in low-fluorine material after fusion with sodium carbonate.³⁷

(2) Azophenylarsonic Acid Field Test.⁷⁸ A field test for the detection of toxic and dangerous concentrations of fluorine has been developed which is especially good in the range of 1 to 10 ppm. Since some inorganic compounds of fluorine are gaseous, an estimation of the concentration is required within a few minutes so that health and safety requirements may be met. Sodium alizarinsulfonate and zirconium chloride were not so satisfactory as *p*-dimethylaminoazophenylarsonic acid and zirconyl chloride. In a solution of a dilute mineral acid, a brown insoluble zirconium azophenylarsonate is deposited in the pores of a Whatman No. 41-H filter paper. Excess free *p*-dimethylaminoazophenylarsonic acid is then washed out by the mineral acid. When fluorides are drawn through the prepared paper, a colorless fluozirconate ion and the free red azophenylarsonic acid are formed. The gas is drawn through the paper by means of a 50 ml capacity pump. A rather accurate estimate of the fluorine concentration may be obtained by evaluating the degree of coloration of the test paper and the number of pump strokes required to produce such coloration. If intense coloration does not occur after 18 strokes, the concentration is less than 3 ppm. Fluoride concentrations from 6 to 10 ppm can be determined within 1 ppm, but with decreasing sensitivity as the concentration increases to 40 ppm. At 2 ppm it may be estimated within 0.2 ppm.

(3) Azophenylarsonic Acid-Acetone Extraction Method.⁵⁶ This method is similar to the field test described above. In the preceding test an element of doubt exists because of the continued presence of brown zirconium azophenylarsonate after the red azophenylarsonic acid has been formed. The free acid is soluble in acidified acetone, whereas the salt is insoluble. The acid can be extracted from the initial spot by acidified acetone. The extract is transferred to a Yogoda confined-spot paper and is evaporated to give a red spot. The intensity of this spot is compared with a series of spots prepared from samples of known fluoride content.

This method can be used in the range of 1 to 500 ppm by volume of fluorine, or in equivalent quantities of other gaseous fluorides, with an accuracy of about 10 per cent.

(4) Ferric-Salicylic Acid Method. This method utilizes the decolorization of the ferric-salicylic acid complex by fluoride ion.^{46,79,80}

The presence of uranyl ion interferes with the bleaching action of fluoride. The effect on the transmittancy depends principally on the amount of uranyl ion present rather than on the ratio of uranyl ion to

fluoride ion. Above 100 γ of uranyl ion per milliliter the effects appear to be proportional to the amount. A linear extrapolation of corrections due to the presence of as much as 200 γ per milliliter at a given fluoride concentration has yielded good results. The amount of uranium present can be estimated by comparing the color that is produced when a potassium ferrocyanide solution is added with the colors of a series of solutions containing known amounts of uranyl ion.

Cobalt(II), bismuth(III), arsenic(III), antimony(III), aluminum, tartrate, citrate, borate, silicate, oxalate, sulfate, acetate, phthalate, and phosphate ions interfere with the test.

Cresotinic acid (and probably other orthophenolic acids) may be used instead of salicylic acid. The ferric-cresotinic acid reagent appeared to be somewhat more sensitive to fluoride than the corresponding Ferrisal complex. Salicylic acid was chosen because it is more readily available commercially in a reagent-grade quality.

A photoelectric colorimeter⁸¹ (see Chap. 24) has been constructed which makes use of the Ferrisal reagent to determine the amount of uranium hexafluoride that has been discharged into the air, by measuring the amount of fluoride in the air. It is sensitive within 0.1 to 10 γ of uranium per liter of air.

Procedure.⁴⁶ A stock reagent solution containing 0.030 mg of ferric ion and 0.137 mg of salicylic acid per milliliter is prepared and stored in a glass-stoppered amber bottle. The pH of the solution should be adjusted to 3.1. This solution has a deep-violet color; its transmittancy at 530 $m\mu$ is 14.2 as measured against water by a Beckman quartz spectrophotometer using 10-mm Corex cells. A standard solution is prepared from the stock solution by diluting 30 ml of the stock solution with 10 ml of hydrochloric acid solution of pH 3.1. The transmittancy of this solution is approximately 23 per cent at 530 $m\mu$. The reagent can be used in the range of 1 to 140 γ of fluoride per milliliter. The reagent can be made sensitive within as little as 0.1 γ per milliliter, with a consequent decrease in range. The range can be extended approximately fivefold by using larger concentrations and a higher ratio of ferric ion to salicylic acid. The more concentrated the reagent is, the less sensitive it is.

In analyzing gases containing fluoride the gas mixture is allowed to flow for a known time interval at a definite rate of flow through a capillary tube. The capillary is immersed in a liquid-nitrogen bath, and any condensable fluoride that may be present is condensed in the U-shaped capillary. This capillary is removed from the gas system, and HCl of pH 3.1 is added to both ends of the capillary in order to prevent the loss of volatile fluorides. The solid in the capillary is melted by immersion in water at room temperature, whereupon it

dissolves in the HCl. The contents of the tube are gently blown into a 25-ml test tube that has been calibrated and constricted at the 5-ml mark. The U-shaped capillary is rinsed several times with HCl, and each washing is added to the test tube. The solution in the test tube is then diluted with HCl of pH 3.1 to the 5-ml mark, and 15 ml of

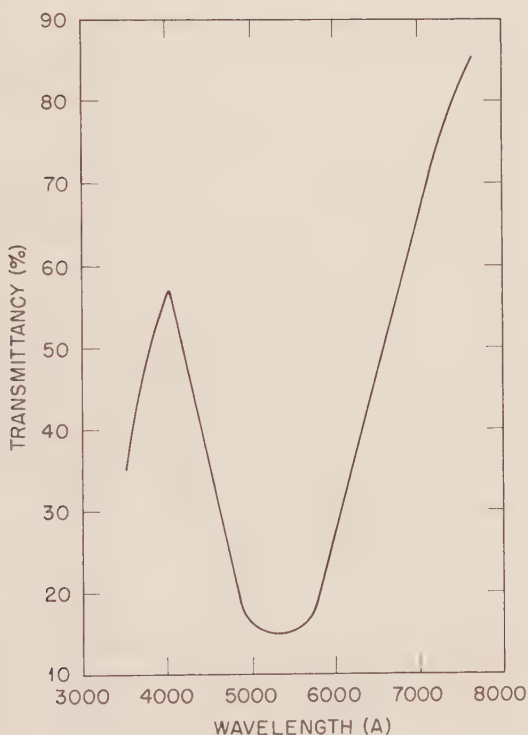


Fig. 5.5—Spectral transmittancy of Ferrisal stock solution.

Ferrisal stock solution is added. The transmittancy of the Ferrisal standard solution is then determined relative to the fluoride-containing Ferrisal solution. (Fig. 5.5 shows the spectral transmittancy of the above Ferrisal stock solution. A wavelength of 530 $m\mu$ was used for the determination of fluoride.)

(5) Bromine-displacement Method.^{51,52,54} The bromine displaced by passing fluorine over heated sodium bromide may be determined colorimetrically. The method may be modified to give continuously and automatically recorded data.

A gaseous mixture of nitrogen and fluorine is passed through a tube containing analytical-reagent-grade sodium bromide, which is heated to 150°C. Below 125°C the reaction is incomplete, and above 200°C some sintering of the sodium bromide takes place. The possibility also exists of a reaction between the bromide and any oxygen that may be in the gas stream with the liberation of bromine, but the reaction with oxygen will not occur below 175°C.

A wide peak in the spectral transmittancy curve for bromine vapor occurs between 400 and 430 $m\mu$. Therefore a photoelectric colorimeter with a 425- $m\mu$ filter is satisfactory. If visual work is required, a wavelength of about 510 $m\mu$ gives satisfactory results.

An absorption cell having a light path of about 25 mm is suitable for the 0 to 10 per cent fluorine range at 425 $m\mu$. Such a cell is also satisfactory for the 10 to 20 per cent concentration range if 525- $m\mu$ radiation is employed. Measurements at 425 $m\mu$ are reproducible within 2 per cent.⁵² For accurate work a pressure stabilizer is required.

(6) Congo Red Visual Method.⁸² Soda lime granules (14 to 20 mesh) are colored red with 0.25 per cent Congo red solution in distilled water and 95 per cent ethanol (1 to 1). After they are dried, the granules may be placed in tubes through which a gas stream flows. Hydrogen fluoride causes a change in color from red to blue. These Korosorb-filled tubes have been used, in general, in the same manner as indicating Drierite and alumina. The soda lime will of course pick up other acidic gases.

(e) Fluorometric Method. The green fluorescence observed when ultraviolet light is passed through a solution containing aluminum ion and morin is quenched by the presence of fluorides.^{38-42, 116} It was found that carefully purified morin (3,5,7,2',4'-pentahydroxyflavone) is less fluorescent in the presence of aluminum than is the original fustic wood extract. If varying amounts of fluoride are added to solutions containing the same amount of aluminum-morin, the fluorescence of the resulting solutions is found to be a function of the amount of fluoride added. The method yields results that are reproducible to ± 20 per cent of the fluoride concentration in the range between 0.005 and 0.05 γ per milliliter. Fluoride concentrations greater than this range can be determined by increasing the aluminum concentration. Gallium and zinc give fluorescent salts with morin. Arsenates, phosphates, and sulfates decrease the fluorescence just as fluorides do. Chlorides and perchlorates do not interfere in concentrations less than $1 \times 10^{-3}M$. In concentrations greater than $1 \times 10^{-3}M$ perchlorate does interfere. Nitrates do not interfere. All interfering substances except sulfate can be eliminated by the distillation of hy-

drogen fluoride from a sulfuric acid solution. The fluorescence will be decreased by sulfate if it is present in concentrations greater than $1 \times 10^{-5}M$.

It was found that the wavelength of light necessary to excite the aluminum-morin fluorescence is very close to the $436\text{-m}\mu$ line of mercury; the resulting fluorescence is green. A Corning No. 5543 filter is placed between the radiation source (a mercury lamp) and the solution, and a Corning No. 3385 filter is placed between the solution and the barrier layer cell of a Klett fluorometer, model 2070. This instrument simultaneously measures the fluorescence of a sample and of a fluorescence standard. Uranium-glass tubing has been found to be a satisfactory, stable fluorescence standard.

For a constant aluminum concentration there is a concentration of morin at which maximum fluorescence is present. The amount of morin is not very critical in this optimum region, so that small errors in the amount of morin added have no effect.

Since the calibration curve is not reproducible, a new curve must be prepared for each set of samples.

(1) Morin Solution. Fifty grams of fustic extract (American Dye-wood Co.) is dissolved in 300 ml of acetone and is filtered. The filtrate is evaporated to dryness and redissolved in 50 ml of acetone. The solvent is evaporated in a vacuum desiccator. The residue is dissolved in 1 liter of 95 per cent ethanol. To 2,800 ml of 95 per cent ethanol, 500 ml of 0.2N acetic acid and the proper amount of the morin solution, prepared as above, are added. The minimum amount of the morin solution needed to produce the maximum fluorescence in a blank is determined for each sample of fustic extract. Usually 200 ml is sufficient.

Procedure.³⁹ To each of several known amounts of fluoride ranging from 0.1 to 0.5 γ in 10-ml stoppered pyrex mixing cylinders, 1 ml of the aluminum solution (0.25 γ of Al, from potassium alum, per milliliter of solution) and 1 ml of 0.2N acetic acid are added. Then 1 ml of the morin solution and 5 ml of 95 per cent ethanol are added, and the solution is brought to a total volume of 10 ml with redistilled water. After mixing thoroughly the solution is allowed to stand for 15 to 20 min before measuring the fluorescence. The fluorescence is plotted against fluoride content.

The samples to be analyzed are treated in the same manner, and the amount of fluoride present is estimated by means of a calibration curve.

(f) Polarographic Method. Fluorine has been determined polarographically by a precipitation reaction in which thorium fluoride is formed.^{83,84}

Thorium ions are not reduced at the dropping-mercury electrode, but they have the property of carrying to the cathode nitrate ions that become reduced there, giving a half-wave potential of approximately 1.3 volts. Investigation has shown that the wave height is proportional to the thorium concentration. Titrations can therefore be carried out by impressing a potential considerably above the indicated potential; a potential of 1.6 volts was chosen.

It was found that the following conditions were desirable in carrying out these titrations. The concentration of the thorium nitrate solution that is used to titrate the fluoride solutions should be 10 to 20 times as great as the fluoride-ion concentration. The volume of the solution should be adjusted so that the fluoride-ion concentration is in the range of 0.002N to 0.006N when titrating with 0.07N thorium nitrate. This solution should also be 0.1N with respect to the supporting electrolyte, potassium chloride, and it should be 10 per cent by volume with respect to ethanol. To fulfill these conditions samples containing 5 to 200 mg of fluorine would ultimately have to be made up to volumes of 100 to 2,000 ml, respectively.

Procedure.⁸⁴ The fluorine may be separated from a sample by distillation [cf. Sec. 1.3c(2)].

The pH of the distillate is brought to approximately 8 with 0.1N NaOH. This solution is transferred to a 1-liter volumetric flask, 100 ml of 95 per cent ethyl alcohol and 100 ml of 1N KCl are added, and the mixture is made up to 1 liter. Exactly 50 ml of the solution is transferred to the titration cell. Oxygen-free nitrogen is bubbled through the solution for 15 to 30 min to remove all dissolved oxygen, and a current measurement is made with the nitrogen diverted through the upper arm of the cell. The 0.07N $\text{Th}(\text{NO}_3)_4$ solution is added to the unknown solution in 0.5-ml increments from a 5-ml buret, a current measurement being made at the end of each addition after nitrogen has been bubbled through the solution for 1 or 2 min. After the end point has been passed, the $\text{Th}(\text{NO}_3)_4$ solution is added in three 0.25-ml increments, the current measurements being made as above. The galvanometer must be shunted with 100 to 1,000 ohms resistance when making current measurements after the last three $\text{Th}(\text{NO}_3)_4$ additions, since the fluctuations of the galvanometer due to the dropping-mercury electrode become especially large after the end point has been passed. The current readings are then plotted against the number of milliliters of $\text{Th}(\text{NO}_3)_4$ solution added. It should be possible to draw two straight lines through the points. The number of milliliters of $\text{Th}(\text{NO}_3)_4$ solution corresponding to the intersection of these two lines represents the end point. The $\text{Th}(\text{NO}_3)_4$ solution can be standardized by titration of a 0.005N fluoride solution made up by

weighing out the appropriate quantity of reagent-grade sodium fluoride. This solution must also be 0.1M with respect to KCl and 10 per cent with respect to ethyl alcohol.

Fluoride has also been determined polarographically by the removal of the catalytic wave of uranium in a nitrate solution by fluoride.^{85,86}

A method has been described for the determination of nitrate by the catalytic wave produced by nitrate in a uranium solution at the reduction potential of quadrivalent uranium.⁸⁷ (Cf. the chapter on electrometric equipment and techniques.) This catalytic wave is removed by fluoride ions,⁸⁸ probably owing to the formation of a uranium-fluoride complex. An unknown fluoride solution is titrated with a standard uranyl acetate solution amperometrically. The sensitivity of the method is 1 γ per milliliter, with an average deviation of ± 7 per cent.

(g) Enzymatic Method. The specific inhibition of enzymatic activity by fluoride ion has been used as a quantitative determination for fluoride.⁵⁸ The hog-liver esterase hydrolysis of ethyl butyrate is inhibited by fluoride ion. The amount of butyric acid formed can then be determined by direct titration with alkali.

The useful range is 0.01 to 0.5 ppm of fluoride. The range can be extended to 10 ppm by the addition of 174 ppm of zirconium as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. It is believed that other substances capable of forming a slightly dissociable complex ion with fluoride would serve as well. The method is accurate within ± 5 per cent for buffer-free solutions. Uranium may be present up to 50 times the amount of fluoride without inhibiting the enzymatic activity. Sodium chloride does not interfere, but carbonate and other ions with a buffering activity do interfere.

(h) Spectrographic Method. There has been little development of spectrographic methods for fluorine because of the lack of sensitivity in ordinary spectrographic methods. Fluorine is detected spectrographically only with great difficulty, because the presence of other elements with lower ionization potentials diminishes the excitation of the fluorine, and because the principal spectral lines lie below 2000 Å, thereby requiring the use of vacuum spectrographs. The *raies ultimes* are at very short wavelengths: singly ionized fluorine has four lines near 950 Å; doubly ionized fluorine has six lines near 605 Å; triply ionized fluorine has two lines near 655 Å; and quadruply ionized fluorine has five lines near 680 Å.^{89,90}

The most sensitive line in the near infrared is at 6856 Å and is due to singly ionized fluorine. This line is a quasi-resonance line. By using the ratio of the intensities of this fluorine line to the intensities

of helium lines, values at the lower concentration limit, 1 ppm, were found to be reproducible within ± 6 per cent.

A hollow cathode source was found to be most satisfactory for emission lines in the near-ultraviolet, visible, and near-infrared regions. The hollow cathode consists of a stainless-steel cathode with water-cooled support. A water-cooled anode was connected to the cathode by a pyrex tube. All the metal parts except the cathode were of brass. Care must be taken to avoid fluoride-containing fluxes if the parts are silver-soldered. The arc was operated at 800 volts and 0.2 amp. The burning period for the visible and infrared regions extended over several minutes.

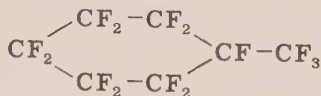
Fluoride concentrations as low as 1 ppm in uranium metal were detected. The lowest absolute sensitivity, 0.01 γ of fluoride, was obtained with a Zeiss low-dispersion glass spectrograph. The greatest concentrative sensitivity was obtained with a 35-ft concave-grating spectrograph with a Wadsworth mounting. In this case the sensitivity limit was slightly less than 1 ppm of fluorine, and the absolute sensitivity was 0.04 γ of fluorine.

Absorption-spectrum methods were considered, but they were not expected to be sensitive or reliable enough to compete with the emission spectra.⁹¹

2. FLUOROCARBONS

By F. E. McKenna, H. F. Priest, and E. Staple

Two main classes of fluorine-containing organic compounds were prepared on the Project: completely fluorinated materials and polymeric chlorofluorocarbons. A system of nomenclature was suggested,⁹² but it was not generally followed or enlarged upon. Many of the terms that appear in the Project literature as applied to pure fluorocarbon compounds are ambiguous, if not incorrect. In this chapter the following convention has been followed: a molecule, such as $\text{CF}_3-(\text{CF}_2)_5-\text{CF}_3$, in which no double bonds appear and in which all the hydrogen atoms have been replaced by fluorine atoms, is called "perfluoro-*n*-heptane." A cyclic derivative, such as



is described as "perfluoromethylcyclohexane," that is, as a derivative of the saturated ring structure rather than as a derivative of toluene.

The prefix "perfluoro-" is used to indicate complete fluorination of the reference compound. The name of the fluorocarbon is based on the parent substance of the fluorinated product rather than on the starting material. The prefix "fluoro-" is considered to be a higher chief function than the prefix "chloro-," unless simplification in naming is obvious.

In addition to methods for the determination of fluorine, methods are also described for the determination of other constituents of fluorocarbons.

2.1 Methods of Determination. (a) Carbon and Halogen Content. The principal problem in the determination of fluorine in organic compounds is the quantitative decomposition of the compound to yield inorganic fluoride. This decomposition is particularly difficult to accomplish because of the high bond energy of a carbon-fluorine bond. To a somewhat lesser extent this situation is true of organic compounds of the other halogens as well.

Many methods commonly used for the decomposition of organic compounds are not adequate for the transformation of organically bound fluorine to fluoride ion, even though these methods yield satisfactory results for the other halogens. Elving and Ligett⁹³ have summarized the decomposition methods previously used. Some of these methods have been modified in Project laboratories to give more satisfactory results. In other instances new methods have been developed for the determination of carbon and chlorine as well as of fluorine.

(1) Simultaneous Determination of Carbon, Fluorine, and Chlorine by Combustion.¹⁶ A combustion train has been developed so that carbon, fluorine, chlorine (and bromine) can be determined in one sample, provided the compound does not contain hydrogen. After decomposition of the compound at 1000°C in a stream of oxygen in the presence of platinum and crushed quartz, the chlorine reacts with silver in an absorption tube at 295°C. Bromine, if present, will also react with the silver. This reaction is quantitative, so that the weight gain in such a case represents the sum of bromine and chlorine present. Fluorine reacts with the quartz to form silicon tetrafluoride, which is then adsorbed on alumina at 175°C. Carbon dioxide is absorbed by Ascarite, as in the conventional determinations of carbon and hydrogen.

The carbon in the sample can be determined within ± 0.3 per cent of the total carbon content. The fluorine may be determined within ± 0.4 per cent, and the chlorine within ± 0.9 per cent, of their respective values.

Hydrogen should not be present in the sample, because water formed in the combustion may be absorbed by the alumina. If the hy-

drogen content is known, it may be possible to correct for this additional weight gain.

Procedure.¹⁶ A combustion train, as shown in Fig. 5.6, is set up as in the Pregl^{94,95} method for the determination of carbon and hydrogen. The quartz combustion tube is 69 cm long and 11 mm in outside diameter (7 mm inside diameter), with a side arm of 6 mm outside diameter (2 mm inside diameter) and a capillary tip 3.5 cm long and 3.5 mm in outside diameter (2 mm inside diameter). The combustion tube is filled with alternate zones of crushed quartz and 3.5-cm-long

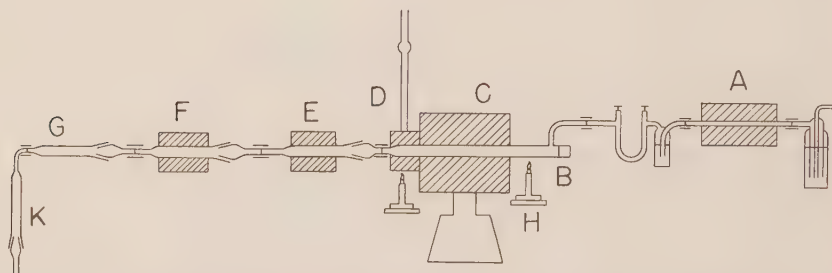


Fig. 5.6—Combustion train. A, purification-train furnace; B, combustion tube; C, combustion-tube furnace; D, furnace; E, furnace; F, furnace; G, carbon dioxide tube; H, burner; K, absorption tube.

coils of platinum gauze, beginning with a roll of gauze at the entrance to the high-temperature furnace and the 7-cm-long 175°C furnace, D, which follows and surrounds the exit end of the combustion tube. Four more rolls of platinum are spaced evenly through the high-temperature region of the combustion tube, alternating with the fillings of crushed quartz previously mentioned.

The silver-filled chlorine absorption tube is attached to the combustion tube by a rubber connection in the conventional manner. The tube is of soft glass, 31 cm long, and it is filled with 2- to 4-mm lengths of clean silver wire packed as tightly as possible. The filled portion of this tube is surrounded by a furnace, E, 21 cm long, which is maintained at 295°C.

The SiF_4 absorption tube is of soft glass, 31 cm long, and it is filled with activated alumina, sodium fluoride, and Drierite. This filling is arranged so that the alumina is at the entrance of the absorption tube and is completely surrounded by the 17-cm-long 175°C furnace, F. Next follows a zone of sodium fluoride, which serves to separate the hot alumina from the Drierite-indicating type and also serves to remove any HF that may pass through the alumina. The

Drierite, which is placed at the exit end of the absorption tube, retains any moisture desorbed from the alumina as a result of the reaction with the silicon tetrafluoride. It is essential that all the alumina be heated before use, because alumina tends to absorb carbon dioxide at lower temperatures.

The third tube, G, is the carbon dioxide tube. It is of soft glass, 20 cm long, and is filled with Ascarite.

A safety tube containing Ascarite and Drierite is used at the end of the train and serves as a connector to the Mariotte bottle, which is used as in the conventional Pregl train.

All these connections are glass to glass and are held in place by heavy-walled paraffin-impregnated rubber tubing.

A 20- to 30-mg sample is used. It is weighed in a micro platinum boat if it is a solid (or a liquid with low vapor pressure). If it is a liquid with high vapor pressure, the sample is weighed in a micro capillary tube.

The absorption tubes are wiped according to conventional micro technique, weighed, and connected to the combustion train in the order described. The furnaces are allowed to come to temperature while the absorption tubes are in place. The zone of the combustion tube into which the sample is to be placed is cooled by placing a moist chamois on the outside of the tube. With the oxygen flowing through the system at the rate of 10 ml per minute, the sample is introduced into the combustion tube. If the sample has been weighed in a boat, it is introduced into the combustion tube at the proper point, and the combustion tube is immediately stoppered. If the sample has been weighed in a glass capillary, a scratch is made at one end of the tube with a file. The capillary, contained in a platinum boat, is then inserted in the combustion tube. The capillary is broken by applying pressure near the scratch. The stopper on the combustion tube is replaced immediately. The wet chamois is then removed from the outer surface of the combustion tube.

A micro burner with a low flame is placed about 3 in. below and 1 in. behind the sample. The burner is moved forward slowly until the sample distills out of its container. A wire gauze is then placed around the part of the combustion tube that contains the sample. The gauze is heated with the largest flame obtainable from the micro burner. Gauze from the boat to the furnace entrance is strongly heated by the flame. After complete vaporization of the sample the oxygen flow is maintained for 20 min.

When the combustion cycle is complete, the absorption tubes are allowed to cool for 20 min after removal from the train. They are then wiped and weighed.

The weight increase in the silver-filled tube equals the weight of chlorine (and bromine, if present) in the sample. Because of the small surface of the silver wire the tube must be repacked after about four determinations. The silver does not absorb any fluorine-containing compound.

The weight increase in the alumina tube equals the weight of SiF_4 absorbed. It is essential that the temperature of this tube be maintained at 175 to 180°C, because the alumina will pick up 25 to 75 per cent of the carbon dioxide at room temperature. If hydrogen is present in the compound, the water that is formed will be picked up by the alumina or Drierite in the alumina-containing tube. If the hydrogen content has been determined by some other method, the weight of water expected from the hydrogen can be subtracted from the weight gain of this absorption tube. When both hydrogen and fluorine are present, some HF is apparently formed, because the capillary tips of the tube containing the silver wire have become etched. What effect this condition has on the analytical results could not be determined, because a pure hydrogen-containing halocarbon was not available.

The gain in weight of the Ascarite-filled tube equals the weight of the carbon dioxide, and the percentage of carbon is calculated directly from this value.

(b) Fluorine and Chlorine. (1) Determination by Fusion with Potassium. Compounds that contain two or three fluorine atoms on a single carbon atom are particularly resistant to decomposition. Elving and Ligett⁹³ have used a fusion with potassium for 30 min at 400°C in a sealed pyrex tube. It was found by Kimball and Tufts¹⁵ that these conditions were not vigorous enough for the quantitative decomposition of some compounds and that prolonged heating resulted in extensive attack on the glass tubes. Use of Corning alkali-resistant glass permitted a decomposition at 450°C for 2½ hr, but high values for the fluorine content were obtained.

Use of a specially designed nickel bomb and temperatures of 500 to 550°C for 2 hr resulted in quantitative decomposition. Chloride was determined by the Volhard method. Fluoride was distilled as fluosilicic acid and then titrated with thorium nitrate.^{17, 96, 97}

The distillation of microamounts of fluorine is successful, because a recovery of 90 per cent when only a few parts per million are present is quite satisfactory. However, when a compound containing 20 to 80 per cent fluorine is analyzed, such a loss cannot be tolerated.

Apparatus. Details of the construction of the decomposition bomb are shown in Fig. 5.7. Before use, the steel parts, C and D, of a new bomb should be heated slowly in a muffle furnace until they acquire a

blue oxide coating. The threads and bearing surfaces between the steel and nickel are kept lubricated with grease and graphite.

The gasket employed between the polished nickel faces of the cover, A, and the cup, B, is a single $1\frac{3}{8}$ -in. circle of heavy waterproof cellophane. When the closed bomb is heated, the differential expansion of the nickel and steel increases the pressure between the sealing faces as the gasket carbonizes, thus ensuring a perfect seal, with no tendency for the faces to stick or seize.

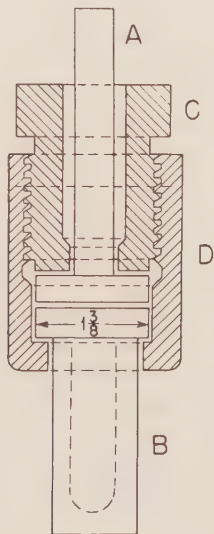


Fig. 5.7—Decomposition bomb. A, bomb cover; B, bomb cup; C and D, bomb holders.

After charging and assembling the bomb to finger tightness, the steel socket nut, D, is held in a vise or suitable bench jig, and the inner nut, C, is tightened with a 16-in. wrench. To open the bomb, the inner nut, C, is loosened a part turn, and A and B are gently tapped to break the seal before removing C and D. This procedure safely releases any small pressure that may be present, without risking the loss of the sample.

The reflux apparatus used for the removal of excess potassium with methanol consists of a strong pyrex cylinder resembling a large test tube, 5 cm in diameter and 17 cm long, large enough to hold the nickel bomb cup, B. The cylinder is closed with a large rubber stop-

per, into which a straight 40-cm reflux condenser is inserted. The cylinder is heated on a steam bath.

The usual laboratory electric muffle furnace, with heat control and temperature indicator and with inside dimensions 3 by 4¼ by 10 in., is adequate.

Procedure.¹⁵ Ordinary solid or liquid samples are weighed in a No. 3 gelatin capsule, with a tight cover. Very volatile liquids can be weighed in a glass ampoule, which, because of the reaction of potassium with glass, should be so thin as to reduce the amount of glass present. For gases the ampoule bulb is blown in the center of a capillary tube and is cooled with dry ice, while the gas is slowly drawn through it until sufficient material has condensed in the bulb. The sample size depends only on the fluorine content and does not take into account the chlorine content. The sample should be between 0.10 g, for materials of high fluorine content, and 0.35 g, for materials of low fluorine content.

The bomb is cleaned and dried. About 1 g of clean pieces of potassium is cut under light petroleum ether. The pieces are quickly dried by evaporation and dropped into the bomb cup, B. The cup is closed with a cork stopper, while the sample is weighed in a covered gelatin capsule. After dropping the capsule into the bomb cup, the circle of cellophane is immediately inserted; the bomb is closed and tightened.

The muffle furnace has meanwhile been brought to temperature. The bomb is placed in it and supported in a moderately slanting position in order to prevent the molten potassium from coming in contact with the gasket. The bomb is heated for 2 hr at 500 to 550°C.

After the decomposition period the bomb is cooled, preferably under an air blast. The bomb is opened as described above. This releases any slight pressure that may be present, but the cover, A, is left in place on the cup, B. After 10 ml of purified methanol (4 liters of analytical-reagent-grade methanol is redistilled, after the addition of 10 g of solid NaOH, and the first and last 500-ml portions of the distillate are discarded; a test for chloride should be negative in the fraction collected for use) has been placed in the bottom of the reflux apparatus, it is assembled, and the air is replaced with carbon dioxide introduced through a tube, which leads down through the reflux condenser and extends about an inch below the end of the condenser. After displacement of the air, the condenser is removed and the cup, B, with the cover, A, still in place, is carefully lowered into the reflux cylinder by means of suitable tongs (made by slightly bending ordinary crucible tongs). After removing the cover the reflux condenser is reattached, and the apparatus is again purged briefly with CO₂. The carbon dioxide inlet tube is removed before refluxing.

The apparatus is heated on the steam bath until the methanol refluxes vigorously. As the methanol condenses and runs down inside the bomb cup, the excess potassium is removed safely and quietly. After about 10 min any remaining lumps (which usually enclose potassium and prevent its removal) are broken up by reaching down through the reflux condenser into the bomb cup with a long glass rod. The glass rod is left in place, and the refluxing is continued for an additional 10 min. As the rod is removed, it is washed with 20 ml of water. Again the reflux is continued for 15 min to complete the removal.

The bomb cover, the cup, and the reflux apparatus are rinsed into a 500-ml Erlenmeyer flask with warm water. A rubber policeman is used to loosen any carbonaceous material adhering to the bomb. About 200 to 250 ml of liquid should be collected. To this amount about 1.5 g of solid ammonium bicarbonate and a few boiling beads are added before evaporating to a volume of 75 to 100 ml. This procedure serves several purposes: the methanol and most of the HCN (formed from the gelatin capsule) are removed, potassium hydroxide is converted to carbonate, and any chloride or fluoride remaining from the carbonaceous material is extracted. The solution is filtered into a calibrated 200-ml volumetric flask, and the residue on the filter is thoroughly washed. The volume is made up to 200 ml and shaken to ensure mixing. This solution should be clear and colorless.

The fluosilicic acid is distilled, and the fluoride is titrated with thorium nitrate solution as described above. Chloride is determined by the Volhard method in an aliquot of the clear solution obtained after fusion.

A combined reagent and gelatin capsule blank should be determined for both chloride and fluoride. The gelatin capsules used had no detectable amount of fluoride.¹⁵

(2) Determination by Fusion with Sodium. Simons and Bloch⁹⁸ suggested the decomposition of fluorine-containing organic compounds by fusion with sodium at the red heat of quartz. After fusion the fluoride was weighed as sodium or calcium fluoride.^{13, 99, 100}

(3) Determination by Peroxide Fusion in the Parr Bomb.^{11, 12} The organic compound may be decomposed in a standard Parr bomb by using 8 to 9 g of sodium peroxide and 1.2 g of a mixture of 3 parts of potassium nitrate to 1 part of sucrose. After decomposition of the sample in the bomb the residual inorganic salts are dissolved in water. The fluoride is distilled as fluosilicic acid, the fluoride in the distillate is titrated with thorium nitrate as described previously, and the chloride is determined by the Volhard titration method.

A sample of halocarbon containing approximately 50 mg of fluoride is used (usually 100 to 150 mg of sample) in this method. A precision of 0.5 per cent of the fluorine content and 0.3 per cent of the chlorine content have been reported.¹¹ However, others have reported erratic results,^{15,93} and halogen values have been obtained which indicated the sample to contain 100 to 300 per cent of the halogen sought.¹⁶

(4) Reaction with Sodium in Liquid Ammonia.¹⁴ Burger¹⁰¹ suggested the use of sodium in liquid ammonia for the decomposition of fluorocarbons. Miller et al.¹⁴ used sodium and ammonia at room temperature under pressure because of unsatisfactory results with Elving and Ligett's⁹³ method for certain highly halogenated compounds.

Procedure.¹⁴ Volatile and nonviscous liquids are weighed in ampoules made by drawing out both ends of a 10-mm length of 7-mm pyrex tubing. One end is drawn out to a fine capillary and sealed off about 15 to 20 mm from the main body of the ampoule. The other end is drawn out to a length of 150 to 200 mm and left unsealed. The sample is introduced into the ampoule by heating the main body of the ampoule, then dipping the unsealed end into the sample, and allowing 0.1 to 0.2 g of sample to flow into the ampoule as it cools. The ampoule with sample is weighed and inverted into the open end of a reaction tube containing about 20 ml of liquid ammonia. The sealed tip is broken off, and the sample is allowed to flow into the liquid ammonia. The ampoule and tip are reweighed, and the sample weight is obtained from the difference. Any sample striking the sides of the reaction tube is washed into the liquid ammonia by using 5 ml of anhydrous ether. Viscous liquids are weighed in tared porcelain micro-combustion boats, the boats are placed in the reaction tubes, 5 ml of ether is added to dissolve the sample, and then 20 ml of liquid ammonia is introduced. Solids are weighed by using a weighing tube. The sample is transferred to a reaction tube, and 5 ml of ether is added to dissolve the sample. Samples insoluble in ether are dissolved in benzene, and 20 ml of liquid ammonia is added.

The reaction tubes are cooled down in a dry ice-alcohol bath. After the addition of liquid ammonia about 0.5 g of metallic sodium cut into small pieces is added. The charged reaction tubes are sealed by drawing out the unsealed end to a capillary and sealing the capillary. The tubes are then placed in a shaker for 5 hr or overnight. The tubes are removed from the shaker and cooled in a dry ice-alcohol bath. Tubes are opened by applying a pin-point flame to a spot near the capillary seal and allowing the slight internal pressure to blow out an opening. The capillary tip is broken off and placed in a 500-ml Erlenmeyer flask containing about 35 ml of 95 per cent ethyl alcohol, and the reaction tube is inverted into the Erlenmeyer flask.

When the vigorous action has ceased, the inside of the reaction tube is rinsed with small portions of alcohol and then with hot distilled water, all washings being transferred to the Erlenmeyer flask. If carbonization has occurred during decomposition, the solution is filtered through a fine pyrex fritted-glass filtering funnel to remove the carbon. The samples are then diluted to 250 ml in a volumetric flask.

If chlorine alone is present, the solution is ready for determination directly. If both chlorine and fluorine or fluorine alone is present, the sample is diluted to 250 ml in a volumetric flask, and 100-ml aliquots are taken for the chlorine and fluorine determinations.

For the determination of chlorine the solution is acidified with nitric acid, and an excess of standard silver nitrate solution is added. A 5-ml quantity of a saturated solution of ferric ammonium sulfate and 15 to 30 ml of nitrobenzene are added, the mixture is shaken to coagulate the silver chloride and coat it with a protective coating of nitrobenzene, and the excess silver nitrate is titrated with standard potassium thiocyanate to a pink end point. This procedure is a modification of the Volhard method.

For the determination of fluorine a 100-ml aliquot of the sample is transferred to a 400-ml beaker, 16 to 22 drops of HCl are added, and the solution is neutralized to a methyl orange end point by using dilute nitric acid (1 to 3). Three drops of excess nitric acid are added, followed by 10 drops of glacial acetic acid and 25 ml of a 10 per cent solution of lead acetate (containing 1 per cent acetic acid). After vigorous stirring the solution is allowed to stand for at least 1 hr (preferably longer) in order to allow the complete precipitation of lead chlorofluoride. The precipitate is filtered by decantation through a fine pyrex fritted-glass filtering funnel, is washed three times with a saturated solution of lead chlorofluoride, and is finally washed three times with small portions (5 ml) of cold distilled water. The precipitate is dissolved in the beaker by the addition of 40 to 50 ml of warm 50 per cent nitric acid, the solution is poured through the filter and beaker, and the filter is washed several times with warm distilled water. The chloride in the solution is titrated by the Volhard method, and the fluorine is calculated from the chloride-fluoride ratio of lead chlorofluoride.

(c) Hydrogen Content. The determination of the hydrogen content of fluorinated compounds has been of primary importance, mainly because most of the fluorocarbons have been prepared by fluorination of the corresponding hydrocarbons, but also because it is extremely important that the hydrogen content of such molecules be kept at a minimum. Despite this importance no completely satisfactory method has been found for hydrogen determination, particularly in the low concentration ranges where it is most important.

The hydrogen content of fluorine-carbon compounds has been previously determined by decomposing the organic compound at 700°C in the presence of magnesium.¹⁰² The resultant gas mixture is passed over hot CuO to convert the hydrogen to water; the water is then absorbed by P₂O₅.

(1) Determination by Pyrolysis.¹⁰³ This method involves the thermal decomposition of the fluorine-containing compound at 1300°C and the absorption of the products of pyrolysis. The procedures used depend on the following assumptions: (1) dehydrohalogenation of the compounds is complete at temperatures above 1300°C, (2) no free fluorine is liberated as a result of the decomposition, (3) any free chlorine that is liberated will react quantitatively with potassium iodide to produce iodine, (4) any hydrogen fluoride formed will be absorbed in water to form hydrofluoric acid or will react with glass to form silicon tetrafluoride, which hydrolyzes to form fluosilicic acid, and the fluosilicic acid will hydrolyze in turn to form hydrofluoric acid by heating, (5) dilute solutions of hydrochloric acid, hydrofluoric acid, and hydriodic acid will not be affected by boiling for a short period of time, and (6) chlorine in slightly acidic solution will, on boiling, be reduced to hydrochloric acid by hydrogen peroxide.

The available data are insufficient to evaluate properly the accuracy of the method, but it has been found that for hydrogen contents of less than 0.1 per cent the method is not quite satisfactory as a control procedure, because it has a high blank and is found difficult to use.¹⁰⁴

Apparatus. The assembled apparatus is shown in Fig. 5.8.

The platinum combustion tube, E, is 0.5 in. in inside diameter and 32 in. in over-all length. It was obtained from J. Bishop & Co., Platinum Works. A 1-in. coil of platinum gauze, M, is placed inside the tube. It is supported in the furnace, T, by a McDaniel high-temperature combustion tube, L.

The furnace, T, is the high-temperature master model CTA 2-9 made by Burrell. Accessory equipment consists of a thermocouple, N, a pyrometer, O, a tap transformer, and a safety switch.

A 500-ml Erlenmeyer flask is used for each of the absorption vessels in the absorption train, P and Q. The flask is equipped with a delivery tube made by sealing 16-mm pyrex tubing to 8-mm pyrex tubing. The inlet tube must extend below the surface of the water.

The purification trains are shown at C, D, F, and G. Nitrogen, used to purge the apparatus and to carry the vapors to be decomposed into the pyrolysis zone, is purified by passage through alkaline pyrogallol, C, and is then dried by passage through concentrated sulfuric acid, D. The last trace of oxygen is removed from the nitrogen by copper

gauze, F, heated to 600°C in the furnace, G. H is a Drierite tube; I and K are collars for connection to the combustion tube.

Procedure.¹⁰³ Only solids and liquids have been analyzed; samples weighing between 0.2 and 0.35 g have been used. Liquids boiling below 200°C are weighed into vials made by sealing one end of a 5-cm length of 7-mm pyrex tubing and drawing out the other end into a fine capillary about 5 cm long. The vial is weighed, and the sample is introduced by heating the vial, dipping the capillary tip into the sample,

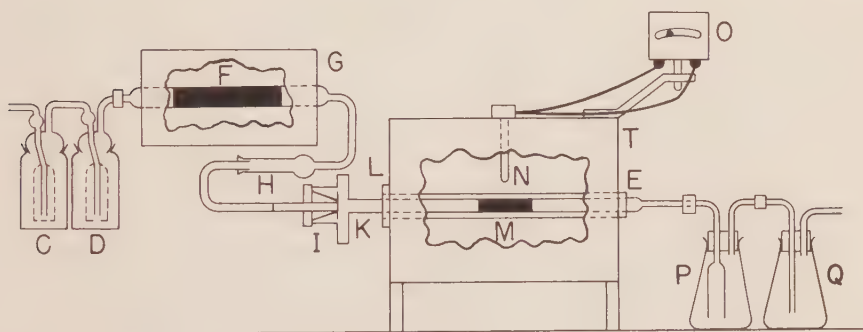


Fig. 5.8—Hydrogen-determination apparatus. E, platinum combustion tube; M, 1-in. coil of platinum gauze; T, furnace; L, McDaniel high-temperature combustion tube; N, thermocouple; O, pyrometer; P and Q, absorption trains; C, D, F, and G, purification trains; F, copper gauze; G, furnace; H, Drierite tube; I and K, collars for connection to the combustion tube.

and allowing the sample to be drawn into the capillary as the vial cools. Materials boiling above 200°C are weighed into a platinum boat.

The platinum combustion tube is moved into the furnace to such a position that about 6 in. of the inlet end of the tube extends from the furnace. Gauze wicks dipping into water are wrapped around each end of the combustion tube about 1 in. from the furnace in order to cool the exposed ends of the tube. This method permits the use of rubber connections for attaching the combustion tube to the rest of the assembly.

When the temperature of the furnace has reached 1300°C, the system is purged with a rapid stream of purified nitrogen for 5 min to force out all the air. The first absorption vessel, containing about 150 ml of redistilled water, is attached to the combustion tube with rubber tubing, and the nitrogen flow rate is adjusted so that 30 to 40 bubbles per minute are formed in the end of the delivery tube. The

delivery tube to the absorption vessel extends just below the level of the water in the vessel. If the ratio of hydrogen to halogen is greater than 1 to 1, chlorine is added along with the nitrogen.

The sample is introduced by opening the inlet end of the combustion tube, shoving the vial, capillary tip first (or the boat containing the sample) into the tube to a point about 2 in. from the open end, and then quickly closing the tube. The remainder of the absorption train is then attached. Low-boiling samples are almost completely volatilized by heat radiated from the furnace. After the pyrolysis is complete, as evidenced by carbonaceous material issuing from the exit end, the cooling wick at the inlet end is removed. The combustion tube is then moved into the furnace, 1 cm each 5 min. After each such move some time is allowed for further reaction. If the sample is introduced in a glass vial, care must be taken to avoid introducing any part of the vial into the furnace. If the sample is introduced in a platinum boat, the tube is eventually shoved into the furnace as far as it can go without burning the rubber connections. The rate of evaporation should be controlled so that a period of about 30 min is required for samples boiling below 200°C and about 45 min for samples boiling above 200°C. This interval is necessary to ensure complete decomposition. When vaporization is complete, nitrogen is allowed to flow for an additional 15 min to sweep all pyrolysis products from the combustion tube. The absorption vessels are then removed, the last vessel being detached first, followed by the first vessel. Finally the first vessel is detached at the combustion tube. It was found that all essential products are collected, as a rule, in the first absorption vessel and that the remainder of the absorption train serves only to absorb the excess free chlorine or other volatile products. Carbonaceous material deposited in the first absorption vessel is removed by filtration through a fine pyrex fritted-glass funnel.

While the solution of the products is being filtered, preparations are made for the next determination. Carbonaceous material is burned out of the tube by blowing through the hot tube.

If fluorine is the only halogen present, the filtrate is boiled for 5 min, and the hot solution is titrated with the standard alkali to a phenolphthalein end point.

If chlorine alone or both chlorine and fluorine are present, the filtrate is diluted to 500 ml in a volumetric flask, and two 100-ml aliquots are taken. To one aliquot is added 1 ml of 30 per cent hydrogen peroxide, and the solution is boiled for 5 min. It is then titrated, while hot, with standard sodium hydroxide to a phenolphthalein end point. The second 100-ml aliquot is placed in an iodine flask, and 10 ml of 6N sulfuric acid and 10 ml of 30 per cent potassium iodide are added. The solution is shaken and allowed to stand closed in the

dark for a period of 10 to 15 min. This solution is then titrated with 0.1N sodium thiosulfate to a starch end point. A blank correction should be made for the 100 ml of distilled water, and the reagents and all titrations are adjusted for this amount. In this case the calculation is as follows:

$$\%H = \frac{(0.001) [(ml \text{ of } NaOH) (N_1) - (ml \text{ of } Na_2S_2O_3) (N_2)]}{(\text{weight of sample}) \times (ml \text{ of aliquot})/500} \times 100$$

where N_1 is the normality of sodium hydroxide and N_2 is the normality of sodium thiosulfate.

(2) Determination by Neutron Scattering.^{105,106} The neutron-scattering cross section of fluorine and carbon is so very low that the presence even of traces of hydrogen, with its large neutron-scattering cross section, in a fluorocarbon can be detected very easily. To obtain the maximum sensitivity by this method it is necessary to have a source of neutrons available which is constant and of sufficient intensity so that a narrow energy band can be chosen. The Columbia University cyclotron was used as the neutron source; no other sources have been tried. This method has been limited in its application because of the need of an almost monoenergetic source of neutrons.

The precision of the neutron-scattering measurements is about ± 0.5 per cent of the hydrogen content. Since the method must be calibrated with known standards, the uncertainty is about ± 0.02 per cent above 0.1 per cent hydrogen and ± 0.5 per cent below 0.1 per cent hydrogen. The method can be applied over the entire range of composition, but it is most sensitive in materials of low hydrogen content. The method has been used for samples containing 2 hydrogen atoms per 1,000 fluorine atoms; this corresponds to about 8×10^{-5} wt. % of hydrogen.

Any hydrogen-containing impurities will contribute to the errors, as will the presence of solids suspended in the sample. Any element with a high neutron-capture or neutron-scattering cross section will interfere seriously. Because of this fact the method is not particularly applicable to chlorofluorocarbons.

Since the cross section of fluorine is smaller than that of carbon and its atomic weight is greater, a change in the ratio of carbon to fluorine will also change the neutron scattering. An increase of 0.10 in the ratio of fluorine to carbon has the same effect as a decrease in the hydrogen content of one hydrogen atom per 1,000 (H + F) atoms. Thus the method is fiftyfold less sensitive to a change in the fluorine/carbon ratio than to a change in the hydrogen/fluorine ratio.

The source of monoenergetic neutrons, adequate neutron counters, and the neutron-beam spectrometer as a collimating device have all

been described by Rainwater and Havens.¹⁰⁶ The absorption cells used to contain the fluorocarbons are made of copper.

A volatile low-molecular-weight fluorocarbon, such as Freon-113, which does not contain any hydrogen atoms, is employed to clean the absorption cells.

Procedure.^{105,106} A source of monochromatic neutrons is produced by bombarding a beryllium target with deuterons from the cyclotron. The neutrons are slowed to the desired energy by paraffin slabs. The neutron beam is monitored before and after passing through the cell containing the sample. Thermal neutrons are removed by a 0.056-cm thickness of cadmium. The procedure is described in detail by Rainwater and Havens.¹⁰⁶

(3) Specific-inductive-capacity Method.^{107,108} This method depends on the direct proportion between the specific inductive capacity of a fluorocarbon and its hydrogen content. Unfortunately the method is not absolute, because a change in structure as well as a change in composition will influence the specific inductive capacity. Therefore a sample having a structure similar to that of the unknown must be used as the standard.

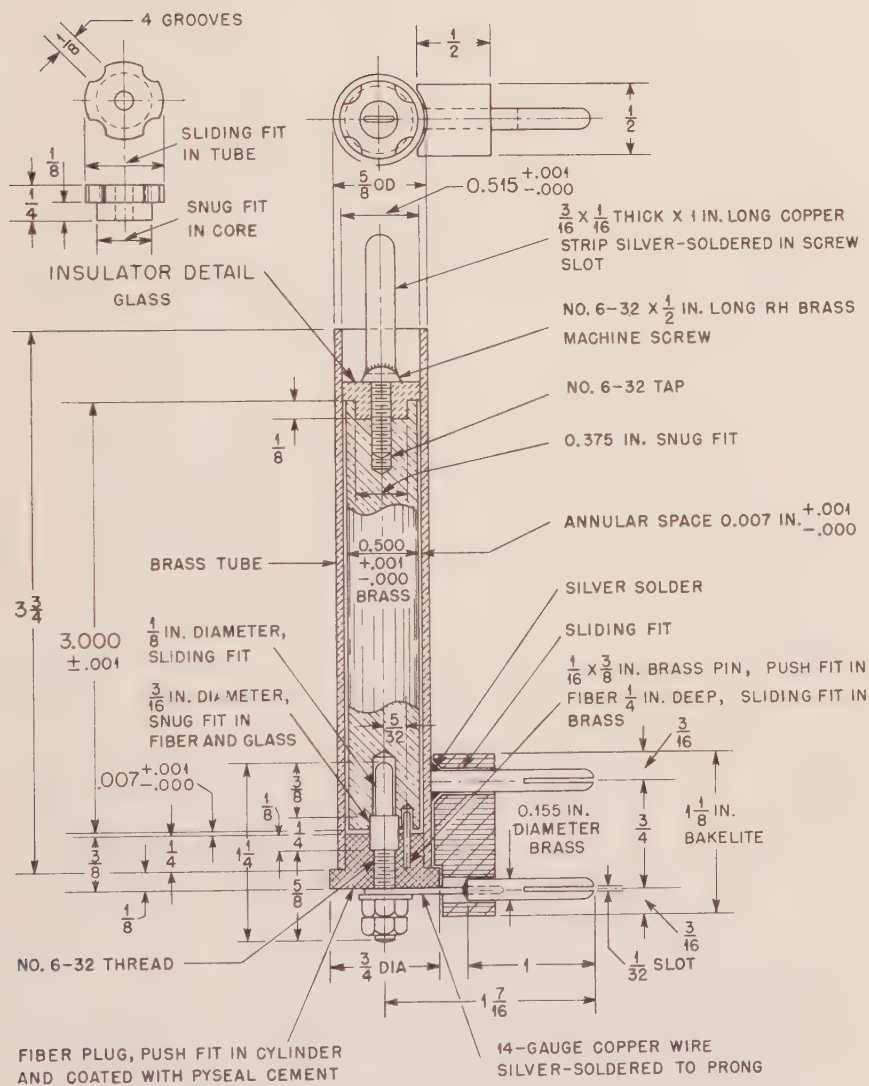
The precision obtainable is of the order of ± 0.01 per cent by weight. The accuracy depends on a knowledge of the hydrogen content of the reference sample. In the range of 0.1 to 5.0 per cent hydrogen the accuracy may be as high as ± 0.02 per cent. Below 0.1 per cent hydrogen this definitely means an accuracy of less than ± 0.05 per cent. The range of the method extends from completely fluorinated compounds to the analogous hydrocarbon.

Suspended solids, dissolved electrolytes, or gases, particularly hydrogen fluoride, all tend to invalidate the results. It is frequently necessary to heat samples of oils to melt and dissolve suspended waxes or higher-melting fractions. Moisture may interfere if it is present in appreciable quantities.

A General Radio type 716-B capacitance bridge, form 455-C, or a bridge such as described by Daniels, Matthews, and Williams,¹⁰⁹ and a cell made from a variable air condenser or by the use of concentric cylinders are adequate.

A hydrogen-free material such as Freon-113, carbon tetrachloride, or C_7F_{16} is needed to rinse the condenser cell.

Apparatus. The capacitance cell consists of an outer shell with an insulating plug in the bottom and an inner cylinder centered by means of a pin in the insulating plug. The upper end of the inner cylinder is centered by means of an insulating collar machined to fit. The annular space that serves as the condenser is approximately 0.005 in. thick, with an inner area of 4.7 sq in. Figure 5.9 shows the details of construction.



DIMENSIONS ARE IN INCHES

Fig. 5.9—Inductive capacity cell.

The housing for the capacitance cell consists of a wooden cabinet 20 in. high, 10 in. wide, and 10 in. deep, with a glass-paneled door. A small ring stand is clamped and screwed down in the cabinet in a stationary position. The electrical adapter for the capacitance cell consists of three double plugs, type 274-M, connected in parallel. Two of these plugs are screwed to a wooden block, which in turn is attached firmly to the ring stand and to the back of the cabinet; the third plug receives the contacts of the cell. The cabinet is wired for a 40-watt light bulb, which generates enough heat to prevent interference from atmospheric humidity. The lead wire from the cell to the capacitance bridge is metal-shielded and insulated.

The capacitance bridge is a type 716-B Schering bridge as supplied by the General Radio Co., with the following accessories for battery operation:*

1. Audio oscillator, type 813A.
2. Amplifier, type 814A.
3. Balancing variable air condenser, type 246L.
4. Headphones, Western Electric, No. 509.
5. Three-volt A battery, 135-volt B battery, 1.5-volt C battery, and 1.5- to 6-volt battery for audio oscillator.
6. Insulated double plugs, type 274-M.

The whole apparatus except the condenser is housed in a large wooden cabinet with a glass-paneled sliding door.

Procedure.^{107, 108} This procedure describes the measurements as made with the General Radio type 716-B capacitance bridge with the two-piece concentric-cylinder cell.

The sample is poured into the cell holder, which is one of the electrodes of the concentric-cylinder type, to a depth of about 0.5 in. The material to be measured must flow freely, and if the sample has a high viscosity, the sample must be heated until it does flow freely. After introduction into the condenser the sample is allowed to cool to approximately room temperature before any measurements are made. The cell is thrust immediately into the holder. This action will cause some of the liquid to overflow, and the excess must be wiped off. Air bubbles must not be in the cell. If, during the cooling, the liquid level drops below the top of the cell, more sample must be added.

The capacitance is measured at 3- or 4-min intervals until three consecutive values check. The temperature of the sample is noted.

*Similar equipment is available for a-c operation.

The sample is removed from the cell, which is then cleaned and rinsed thoroughly with the hydrogen-free solvent. The capacitance of the clean empty holder is measured, as well as of the holder with the cell in place.

The relative specific inductive capacity is calculated as follows:

$$\text{Specific inductive capacity} = \frac{C_x - C_b}{C_a - C_b}$$

where C_x is the capacitance of the holder and cell filled with liquid, C_a is the capacitance of the holder and cell filled with air, and C_b is the capacitance of the holder. All capacitances are expressed in micromicrofarads, and all values are corrected to 30°C by a previously determined temperature coefficient.

The hydrogen content is determined by reference to a calibration curve prepared by determining the specific inductive capacities of samples of known hydrogen content and known structure.

(4) Determination by Refractive-index Measurements.^{110,111} The refractive index and the density of the hydrogen-containing fluorocarbon are measured. By means of the Lorenz-Lorentz expression it is possible to prepare a curve of the fluorine-hydrogen ratio as a function of the specific refraction.

The ratio of fluorine to hydrogen atoms can be determined with a precision of ± 5 per cent. The accuracy is not known. For fluorine/hydrogen values less than 3 some doubt exists as to the constancy of the value of the atomic refraction of fluorine. Thus the useful range of the method is limited. Above this value of the fluorine/hydrogen ratio the following accepted values for the atomic refractions are used: 1.23 for fluorine, 2.418 for carbon, and 1.100 for hydrogen.

Any dissolved impurity that is neither fluorocarbon nor hydrocarbon yet affects the refractive index will cause large errors.

From the theoretical standpoint the measurement of the refractive index of fluorocarbons does not differ from the measurement of the refractive index of any liquid. From the practical standpoint, however, a serious complication arises, because the refractive indices of most fluorocarbons near room temperature are in the range of 1.0 to 1.3. The lower limit that can be measured by most refractometers is about 1.3.

Because of the difficulty of directly measuring the refractive indices on ordinary instruments, a method was used with a hollow prism mounted on a simple spectrometer table. By using a mono-

chromatic light source the prism table is rotated until the position of minimum deviation of the refracted light beam is found. From the incident and emergent angles of the light beam and from the characteristic angles of the prism, it is possible to calculate the refractive index of the liquid.

A 60-deg hollow prism is obtainable from the Klett Mfg. Co. An angular or prism-table type of spectrometer, like the model manufactured by The Gaertner Scientific Corp., may be used to support the prism. The light source is a sodium-arc light or other source of monochromatic light.

Procedure.^{110,111} The density and refractive index of the sample should be determined at the same temperature. For the refractive index measurement the sample is introduced into the clean, dry hollow prism, mounted on the spectrometer table. The prism table and movable telescope are rotated until the image of the slit is located in the telescope at the position of minimum deviation from the path of direct transmission. This angle of minimum deviation, Q , is measured. For a 60-deg prism the refractive index is calculated from the equation

$$n_D^t = 2 \sin \frac{(60 + Q)}{2}$$

The specific refraction is calculated from the equation

$$r = \frac{1}{d} \times \frac{n^2 - 1}{n^2 + 2}$$

where d is the density, r is the experimental specific refraction, and n is the refractive index. The molecular refraction is equal to the specific refraction multiplied by the molecular weight. A calibration curve can be prepared for the fluorine/hydrogen ratio vs. the specific refraction. From this curve the composition of the unknown can be determined.

(5) Estimation by Fluorescence.^{101,112,113} Fluorocarbon lubricants of high molecular weight that contain some unreplaced hydrogen atoms show a greater intensity of fluorescence than do the completely fluorinated compounds. The nature of the fluorescence is unknown.

The accuracy of this method will depend on a knowledge of the hydrogen content of the standard substances used in the calibration of the method. Impurities and structural differences may produce effects that are of greater magnitude than those caused by the hydrogen content. It is important to compare only those samples that have a similar history.

Measurements have been made with a Coleman Electric Company model 12 electronic photofluorometer. A B-1 filter, which has a maximum transmission of $365\text{ m}\mu$, is placed between the light source and the sample. A second filter is placed between the oil and the photocell to remove light of the incident wavelength. If the intensity of fluorescence is too great, a wire-mesh screen may be inserted in series with the filter.

Procedure.¹⁰¹ The samples are placed in the cuvettes, which are furnished with the photofluorometer, and the intensity of fluorescence is determined. If a solid phase is present, a higher intensity will be obtained on account of the reflection from the phase boundaries. It is therefore desirable to warm the samples to 50 or 60°C before measurement in order to ensure a homogeneous liquid phase. Standards of known hydrogen content are run in the same manner, and the hydrogen content is obtained from a calibration curve.

(d) Determination of Water. This method uses the Fischer reagent,¹¹⁴ and the end point is determined potentiometrically according to the method of Almy, Griffin, and Wilcox.¹¹⁵

An accuracy of ± 0.0004 per cent in the range of 0.04 to 0.0004 per cent water may be expected.

A titrimeter such as a Beckman research model pH meter, with a platinum-tungsten electrode assembly, has been used.

Procedure. About 50 g of fluorocarbon is weighed into the titration flask to the nearest 0.1 g. A 25-ml sample of Freon-113 redistilled from KOH is added, and the mixture is shaken until homogeneous. Fischer reagent¹¹⁴ diluted with anhydrous methanol is added until a permanent brown color is obtained. This mixture is shaken for 5 min and then titrated potentiometrically with the methanol-water reagent. The reagent is prepared by dissolving 2 ml of water in 1 liter of anhydrous methanol, and it must be standardized as described by Fischer.¹¹⁴ A 20- to 30-mv change will occur at the end point. A blank should be run on the Freon-113.

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Chapter 6

CARBON, HYDROGEN, AND OXYGEN

By C. J. Rodden

Chemical determinations of carbon and hydrogen made on various materials are discussed in this chapter. Low-pressure methods involving vacuum fusion for the determination of carbon, hydrogen, and oxygen are treated in Chap. 27.

1. RÉSUMÉ OF METHODS

Among the determinations made for the Project was the determination of hydrogen in graphite and in powdered uranium.

The procedure was essentially the same as that used in micro-chemical analysis.¹ A quartz tube with an enlargement was provided to accommodate the large sample required. In the analyses of powdered uranium it was necessary to distinguish between water and hydrogen. This differentiation was accomplished by heating the sample in dry nitrogen at 110°C and weighing the water in an absorption tube filled with Anhydrone. The sample was then burned in oxygen, and the water was absorbed and weighed.² With the advent of fused uranium and the necessary routine determination of carbon and hydrogen, samples were burned in a quartz tube in pure oxygen, and the water formed was absorbed in Anhydrone and the carbon dioxide in Ascarite.³ This method, or a modification of it, was widely used.⁴⁻⁷ This method has been used for the analysis of thorium metal, but the metal must be finely divided.

The determination of carbon dioxide in minerals and ores was carried out according to well-established procedures, utilizing the evolution of carbon dioxide by means of acids. The carbon dioxide was purified, absorbed in Ascarite, and weighed.⁸

The determination of water has been made by various methods. With many materials a determination of the loss at 110°C has been

adequate; but with other materials, such as commercial U_3O_8 and UF_4 , the water is not all evolved at this temperature, and, on heating to higher temperatures, other substances such as sulfuric acid and hydrofluoric acid may be evolved, or the substance may oxidize.

Commercial U_3O_8 has been analyzed by mixing with sodium carbonate, heating to 900°C , and weighing the evolved water after absorbing in Drierite.⁹ In an alternate method the sample is heated to 400°C in a stream of nitrogen in the apparatus used for the carbon and hydrogen determination.³

Uranium trioxide has been analyzed for its water content by igniting the sample in a stream of nitrogen and weighing. The liberated water is absorbed in magnesium perchlorate and weighed.^{10,11}

The determination of the water content of UF_4 was more difficult. Two methods were used. In the first method the sample was heated in a current of nitrogen in a copper tube, the liberated gases passing over hot copper chips and then over hot copper oxide. The liberated water was then absorbed in Drierite and weighed.^{12,13} In the second method the sample was mixed with sodium carbonate and heated to 1000°C while oxygen was passed through the tube. The evolved water was absorbed in Anhydron and weighed.¹⁴ (Hydrogen is included in the weighing if present.)

A novel method for the determination of water in uranyl sulfate depends on the complete thermal decomposition of the salt and the evolution of hydrogen by sodium metal from the sulfuric acid formed in the process.¹⁶

The Karl Fischer method²⁶ for water has been found to be applicable to the determination of water in uranyl nitrate and in an ethereal solution of uranyl nitrate.¹⁷

The oxygen content of thorium metal was obtained by dissolving the sample in hydrochloric acid and boiling the solution until the residue became white. This residue was filtered, washed, ignited, and weighed as thorium oxide, and the oxygen content of the metal was then calculated.¹⁸

2. CARBON AND HYDROGEN

Carbon and hydrogen are separated by converting to carbon dioxide and water, respectively, purifying these products, and absorbing them in suitable absorbents.^{7,19} Since the points to be discussed are principally points of technique, a representative procedure^{7,19} as applied to uranium metal will be given.

2.1 Simultaneous Determination of Carbon and Hydrogen. (a) Apparatus. The apparatus (Fig. 6.1) consists of a pressure-reducing valve and a needle valve on a supply of 98 per cent oxygen gas; two

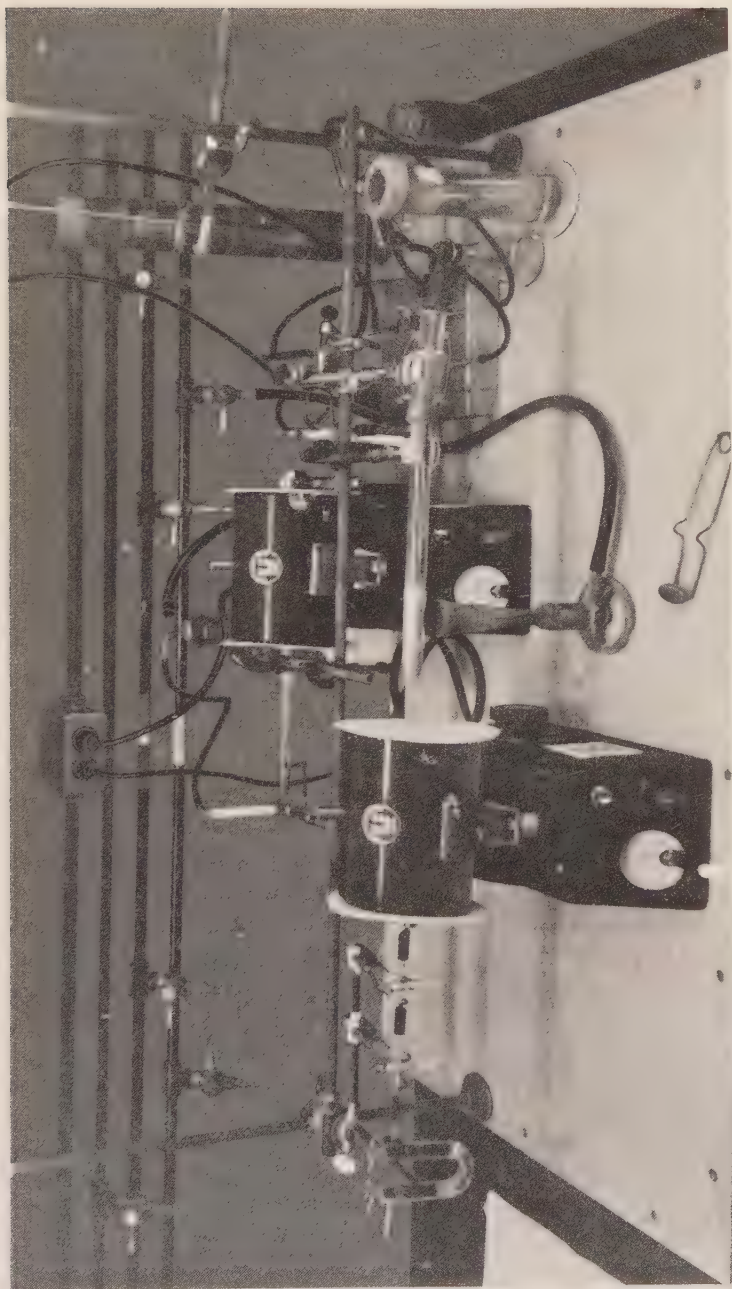


Fig. 6.1 — Apparatus for analysis of carbon and hydrogen.

micro pressure regulators, one twice the size of the other; two three-way stopcocks; a 2-liter safety bottle; a terminal drying tube; a Vycor micro combustion tube; a U-tube bubble counter; a quartz combustion tube with an enlarged combustion chamber; two Friedrich absorption tubes; and a U tube. These are connected in the order listed. All parts of the train are standard microanalytical equipment unless otherwise specified. The oxygen line, pressure regulators, gas safety bottle, terminal drying tube, and Vycor combustion tube are connected with pure gum-rubber tubing. All other connections are made with specially impregnated rubber tubing.

The small pressure regulator is used whenever the stopper of the combustion tube is in place. When this stopper is removed, the larger pressure regulator is used so that there will be enough pressure in the system to effectively prevent any air or moisture from being drawn in at the open end of the tube.

The combustion unit is assembled on a rigid platform 2 by 4 ft. The preheating furnace and Vycor combustion tube are placed parallel to, and in back of, the quartz combustion tube. The U-tube bubble counter is placed perpendicular to the two combustion tubes and connects them. All the pieces of apparatus described above, except the last three tubes, are clamped rigidly to a common iron bar, which runs lengthwise down the center of the platform and is supported on both ends by upright bars bolted to the platform. The carbon dioxide- and water-absorption tubes are suspended from hook clamps so that they may be removed for weighing.

The Vycor combustion tube used for the preheater is filled with copper oxide (in wire form) for a distance of 7 in. from the capillary end and is heated in a micro combustion furnace. The drying tube, which follows the preheater, is filled in the usual manner with Anhydron. The temperature of the furnace is raised to 700°C and kept there continuously, once the train has been assembled. The U tube of the U-tube bubble counter is filled with Ascarite and Anhydron. The Ascarite occupies half the tube, and the Anhydron occupies the remainder of the space. The bubble-counter portion of the tube contains sulfuric acid. The quartz combustion tube (made by Macalaster Bicknell Co.) has a combustion chamber approximately $\frac{7}{8}$ in. in diameter and 11 in. long, and it is closed with a ground-glass stopper. The other end of the combustion chamber is reduced to approximately $\frac{1}{2}$ in. in diameter and is sealed to a tube approximately 10 in. long. The $\frac{1}{2}$ -in. tube is again reduced at the exit end and is sealed to a capillary tube 2 in. long. This combustion tube is filled for a distance of 7 in. from the capillary end with copper oxide wire, which is held in place by small plugs of asbestos fiber.

The section of the combustion chamber in which the sample is burned is wrapped with a piece of platinum foil 2 in. long in order to afford protection from the direct heat of the Fisher burner, which is used in igniting the sample. The section of the combustion tube holding the copper oxide is heated with a furnace of the same type as the preheater.

Both the water- and the carbon dioxide-absorption tubes are standard Friedrich micro absorption tubes. The water tube is filled with Anhydrone held in place by a small cotton plug (or glass wool) in the bottom of the outer tube. The carbon dioxide tube contains Ascarite for two-thirds of the length of the inside tube and Anhydrone in the remaining space. The two chemicals are held in place by small cotton plugs. Glass joints on both the absorption tubes are lubricated with Lubriseal. Care must be taken to ensure complete removal of the excess lubricant from the outside surface of the tubes. The glass stoppers in the U tube at the end of the absorption tubes are likewise lubricated with Lubriseal. The curved portion of the tube is filled with glass beads, and sufficient sulfuric acid is added to cover these beads.

A quartz boat about 10 by 15 by 40 mm is employed for holding the sample in the combustion tube. The boat is given a preliminary cleaning in acid; it is then rinsed in water and ignited in a hot flame. It is not cleaned between runs but occasionally is ignited in a free flame, being handled only with platinum-tipped forceps.

(b) Blank Corrections. During a series of analyses, especially after the train is newly assembled or after any alterations or replacements have been made in the system, blanks must be run to ensure complete freedom from sources of carbon dioxide or water. In determining the blank the empty quartz boat is inserted into the combustion tube, the platinum shield is heated as in the determination itself, and oxygen is passed through the system in the normal manner. It may be necessary to pass oxygen through the system for as long as 24 hr before the system is free from contamination, the length of time depending on the nature of the interruption. The absorption tubes are inserted in the train at suitable intervals to check the carbon dioxide and water content of the oxygen stream leaving the train. The tubes are connected to the train for 20-min periods. The train is swept out until the change in weight of the carbon dioxide tube is not more than +0.05 mg and the change in weight of the water tube is not more than +0.08 mg on two consecutive determinations. The weighings are made in the following manner:

After removal from the train the tubes are carefully wiped, first with a damp flannel cloth and then with chamois. They are set on a rack outside the balance case for at least 10 min. The water tube

(containing Anhydrone) is then placed on the hooks of the left pan of the balance, and the carbon dioxide tube (containing Ascarite) is placed on the floor of the balance at the left side of the pan. A counterpoise flask (previously adjusted with enough lead shot to make its weight approximately 5 mg less than its corresponding absorption tube) is placed on the right-hand pan of the balance, and the tube and counterpoise are allowed to remain in this position for 5 min, with the beam of the balance arrested. The water-absorption tube is weighed first, followed by the carbon dioxide-absorption tube.

Before a sample is tested, a final blank is run on the system. This final blank may be conveniently carried out during the period in which the sample is being prepared for analysis. The stopcocks in the oxygen line are turned so that the large pressure regulator is connected into the system. The glass stopper is removed, and any uranium oxide from previous combustions is removed from the combustion tube and boat. The empty quartz boat is inserted in the section of the combustion tube surrounded by the platinum sleeve. The glass stopper is replaced, and the stopcocks in the oxygen line are turned so that the small pressure regulator is in the system. The absorption tubes are connected to the capillary end of the combustion tube, the burner under the platinum sleeve is lighted, and the system is given a preliminary flush with oxygen for 20 min. The absorption tubes are disconnected from the train and weighed. The value obtained is used as the original weight of the tube for the blank determination.

The stopcocks in the oxygen line are turned so that the large pressure regulator is connected into the system. The glass stopper is cautiously and slowly removed from the combustion tube, and the empty quartz boat is drawn to the opening of the tube. (This partial withdrawing of the quartz boat must not be carried out until at least 10 min after removing the flame from the boat.) The boat is allowed to remain in this partly exposed position for a length of time equal to the time required for transferring the sample to the boat in a regular analysis. Then the boat is pushed back into place in the tube, and the glass stopper is replaced. Next, the stopcocks in the oxygen line are turned so that the small pressure regulator is in the system. The oxygen is allowed to flush the system for 20 min before the burner under the boat is lighted or the absorption tubes are put in the system. This action is carried out during the period in which the absorption tubes are being weighed. The absorption tubes are attached at this point, and the burner is lighted under the boat. Oxygen is passed through the system for 20 min, and then the absorption tubes are removed and weighed.

The increase in weight of the absorption tubes is the value applied as a blank correction in the subsequent analyses during the day. If

the gain in weight of the carbon dioxide tube is greater than 0.05 mg, and if the gain in weight of the water tube is greater than 0.08 mg, the blank must be repeated until acceptable values are obtained. Occasionally, and at least once a week, a second blank is carried out at the end of the day in order to determine whether there has been any appreciable change in conditions of the system during the day.

(c) Procedure. The sample, generally weighing 2 to 2.5 g and made up of several pieces, is placed on a watch glass, and each piece is inspected to ensure the absence of adhering foreign matter. It is then transferred to a 50-ml beaker and washed by vigorous agitation with 95 per cent ethyl alcohol, followed by ether. The washed pieces are transferred with platinum-tipped tweezers to a clean watch glass and dried at 110°C for 30 min. The watch glass is placed in a desiccator, and the sample, when cool, is weighed to the nearest 0.01 g. Contamination of the sample is avoided by taking great care in handling, using clean platinum-tipped tweezers for all transfers of the pieces. The weighed sample is stored in a desiccator until the combustion train is ready for use; however, the cleaned sample must not be stored for a long period, even in a desiccator.

After the preliminary blank corrections have been found satisfactory, the analysis of the sample may be started. The stopcocks in the oxygen line are turned so that the large pressure regulator is connected into the system. The glass stopper is cautiously and slowly removed from the combustion tube, and the quartz boat is drawn to the opening in the tube, but the boat is not withdrawn from the tube. The pieces of the sample are transferred to the boat; delay in the transfer is avoided in order to prevent the absorption of moisture by the sample and the boat. The boat is pushed into place in the combustion tube, the glass stopper is replaced, the stopcocks in the oxygen line are turned so that the small pressure regulator is in the system, and the system is flushed with oxygen at the regular rate for 20 min. Then the absorption tubes are attached, and the burner is lighted under the boat holding the sample.

At the moment that the metal begins to ignite (generally after 2 to 3 min), the stopcock on the sulfuric acid U tube at the exit end of the train is closed, and the oxygen flow is adjusted so that it is always sufficient to ensure complete oxidation of the sample. The time for complete oxidation of the sample varies from 5 to 30 min. Glass blowers' tinted goggles must be worn by the analyst during this period so that he may watch the progress of the oxidation without harm to his eyes.

During the burning period the oxygen pressure is watched and adjusted with extreme care. When the sample is completely oxidized, the stopcock in the exit sulfuric acid U tube is opened, and the oxy-

gen flow is adjusted to normal. The system is swept out for 20 min. The tubes are removed from the combustion train, treated as in the blank run above, and weighed. From the weights of carbon dioxide and water formed (corrected for the blanks on the respective absorption tubes) the percentages of carbon and hydrogen are calculated.

The above procedure, which may appear unnecessarily detailed, must be rigidly adhered to in order to obtain consistent results. It is highly important that the quartz boat used for the metal be kept in the tube and a new one substituted when the boat becomes pitted. A quartz boat that has been etched picks up considerable moisture on exposure to air, even in a short period of time. In one laboratory quartz boats have been replaced by porcelain boats, which last for only one or two determinations but do not give so high a hydrogen blank as a quartz boat that is used continuously. One laboratory found²⁰ that alundum boats were useless in the determination of hydrogen because of their great hygroscopicity. Although the boats were placed in a desiccator as soon as possible after being removed from the furnace (2 to 3 min), they absorbed 10 to 20 mg of water from the air. In the determination of carbon and hydrogen in thorium metal, using the above procedure, it was found necessary to use filings made with a rasp; otherwise, complete burning did not take place.²¹

This procedure, omitting the weighing of the water-absorption tube, has also been used for the determination of carbon in uranium carbide on a semimicro scale.

Many of these details may be dispensed with if only the carbon content of the metal or carbide is desired.

2.2 Determination of Carbon in Uranium and Uranium Compounds. The following procedure describes a method of determining carbon.^{4,6} The apparatus, technique, and weighing precautions greatly resemble those used in iron and steel analysis. The electric furnace, heated to $1100 \pm 100^\circ\text{C}$, holds a quartz tube 2.9 cm in inner diameter and 60 cm long. The oxygen passes from the cylinder through a U tube charged with Ascarite and Anhydrone and then through a flowmeter containing colored mineral oil. The exit of the quartz tube leads to a sulfuric acid-chromic acid bead tube, then through a U tube of Anhydrone to the weighing tube of Ascarite topped with Anhydrone.

Two varieties of alundumware combustion boats now on the market have been employed. For high-carbon materials an alundum tube 20 mm in outer diameter, 13 mm in inner diameter, and 96 mm long was found satisfactory. For low-carbon materials, such as metallic uranium (which expands greatly upon oxidation), the larger boats are necessary. These are 105 mm long, 14 mm wide, and 9 mm deep, with a hemicylindrical lid.

(a) Procedure. The boat selected is preignited in a slow stream of oxygen for 15 min and then cooled in a desiccator. The sample is weighed into it, the size of the sample varying with the carbon content. For carbides (UC_2 or U_2C_3) containing approximately 10 per cent carbon, about 0.5 g is convenient. In the case of low-carbon materials, such as U_3O_8 or metallic uranium, larger samples must be used. Samples of the metal as large as 8 g have been burned without danger, although the reaction is quite violent.

The weighing tube and its tare, wiped carefully with a cheesecloth or chamois, are allowed to stand for 10 min in the balance case and then are weighed to the nearest 0.1 mg.

After the weighed tube has been connected to the train, the boat containing the sample is slowly pushed into the furnace, enough time being allowed to heat it gradually in order to diminish the danger of cracking the tube. The oxygen is passed through at a rate of 200 ml per minute for 1 min or until the sample ignites; the rate is increased to 400 ml per minute for 3 min to prevent drawing air back into the weighing tube. Then the rate is decreased to 200 ml per minute for 15 min, giving a total combustion and sweeping-out time of 18 to 19 min. In the case of U_3O_8 samples, which do not absorb large amounts of oxygen, the rate of 200 ml per minute is maintained for the full 19 min. When large samples of uranium metal are oxidized, the rate must be increased above 400 ml per minute to 600 or 800 ml per minute in order to prevent drawing air back. The weighing tube and its tare are again wiped as before, allowed to stand for 10 min in the balance case, and reweighed to the nearest 0.1 mg.

For very small amounts of carbon dioxide, smaller weighing tubes may be used, but the oxygen rate must be decreased correspondingly. A blank is run, using the same oxygen rate and time as in the oxidation of the sample. The blanks run about 0.3 mg of carbon dioxide.

This apparatus has also been used for the determination of carbon in UF_4 . The results are 2 to 5 per cent high, as determined from the added amounts of uranium carbide.

(b) Procedure.⁴ The UF_4 is dried to constant weight at 110°C , and 0.5 to 1.0 g is weighed out into an agate mortar. An equal weight of magnesium oxide (which was previously ignited at 1000°C in oxygen in a combustion furnace or in air in a muffle) is added, and the two substances are ground together. After brushing into an ignited porcelain boat, the mixture is covered with magnesium oxide and ignited as above, and a rate of 75 ml of oxygen per minute is maintained for 30 min. A blank is run without removing the sample. The blanks usually run about 5 mg or less.

3. WATER

The determination of hydrogen and absorbed water in uranium metal was made in an apparatus similar to the one described for carbon and hydrogen.

3.1 Determination of Water in Uranium Trioxide. In seeking a method for the determination of water in uranium trioxide, it was found that all water was evolved by heating for 10 min at a temperature of 850°C with a nitrogen flow of 3,000 ml per minute. Since the uranium trioxide had been made from nitrate, it was necessary to determine the effect of nitrates. It was found that when more than 100 mg of nitrate ion was present, high results were obtained. This amount of nitrate ion is much higher than is found in uranium trioxide, and therefore no provision was necessary to remove oxides of nitrogen.

(a) **Apparatus.** The apparatus consisted of the following items in the order of the flow of gas through the assembly: a cylinder of oil-pumped nitrogen, with the flow rate controlled by a needle valve; a U tube containing calcium chloride and some indicating Drierite; a U tube containing magnesium perchlorate; a calibrated mercury manometer; a McDaniel combustion tube for high-temperature work—70 cm long, with a bore of 3 cm, and with the outlet end constricted to 0.5 cm—heated by a multiple-type Hoskins combustion furnace controlled by a variable transformer; a double-stopcock U tube of 12 mm bore, containing calcium chloride; and a test tube containing mercury to serve as a safety valve.

(b) **Procedure.**¹¹ A 1-g sample is weighed into a porcelain boat 15 by 100 mm; the boat is then placed quickly into the combustion tube and pushed into the hot section (maintained at 850°C) by means of a metal rod hooked through the lip of the boat. The rod is left attached to the boat. The end of the tube is stoppered, the collector stopcocks are opened, and the gas stream is adjusted to 3,000 ml per minute. After 10 min the gas stream is turned off, the collector cocks are closed, the end of the tube is stoppered, and the collector is removed and weighed.

3.2 Determination of Water in UF_4 . Water in UF_4 has been determined by two methods. One method consisted in heating the sample after mixing with sodium carbonate and then absorbing the liberated water in Anhydrone.¹⁴ Another method consisted of heating the UF_4 in a nickel or copper tube in a current of dry nitrogen and weighing the liberated water after absorbing in a drying agent.^{12,13,20} The initial work consisted of refluxing the sample with Anhydrone, ethanol, and pyridine. The ethanol and pyridine were distilled off, and the distil-

late was titrated with Fischer's reagent.^{22,26} Attempts to determine the water content by heating in a high vacuum were unsuccessful.¹²

For control work, simple drying at 110°C has proved satisfactory. A comparison of results obtained by heating samples in an oven shows that a gradual loss in weight occurs with an increase in temperature,²³ as shown in Table 6.1.

Table 6.1 — Weight Losses in Heated UF_4 Samples

Sample	Percentage loss		
	110°C	125°C	150°C
A	0.014	0.024	0.024
	0.014*		
B	0.020	0.026	0.032
	0.015*		

*Determination made in different laboratory.

Results obtained by heating in a furnace in a current of nitrogen with sodium carbonate showed higher water content than when the sample was heated alone. Carbon dioxide evolution from the UF_4 - Na_2CO_3 mixture was high at 375°C, thus indicating that reaction had taken place. In the loss occurring at the 110°C level and in the copper-tube method any free hydrogen fluoride was counted as water.

For routine control the loss at 110°C is believed adequate, but the possibility of the presence of combined water makes it desirable to use an elevated temperature for special work. In this case the copper-tube method is to be preferred.

(a) Copper-tube Method.¹² Apparatus. The apparatus consists of the following equipment in the order of gas flow: a Vycor tube packed with copper wire and heated to 650°C by a tube furnace; a purification tube filled with indicating Drierite; a copper tube with a side-arm opening for nitrogen (the opening for the boat is closed by a stopper containing platinum baffles, the exit end of the copper tube is filled with copper chips and copper oxide, which are heated to 500°C, and both ends of the copper tube are cooled by jets of air); an absorption tube filled with indicating Drierite; and a U tube containing sulfuric acid and glass beads used to indicate the flow of gas.

Procedure.¹² A 1-g sample of UF_4 is weighed into a platinum boat and introduced into the copper tube with the absorption tube closed, with nitrogen passing out of the tube opening. The opening of the copper tube is then closed. The absorption tube is opened, and the section of the copper tube that contains the sample is heated with a tube

furnace to 500°C. Nitrogen is passed through the system for 1 hr; the absorption tube is then closed, removed from the system, and weighed after 10 min.

In experiments in which the loss in weight of the sample was compared with the increase in weight of the absorption tube, the results were usually consistent.

(b) Sodium Carbonate Method. Procedure.¹⁴ One gram of sample is mixed with 2 g of sodium carbonate (previously heated to 600°C), transferred to a zircite boat lined with alundum, and covered with an additional 2 g of sodium carbonate. The boat is inserted into a tube furnace (where it is heated to approximately 1000°C), through which a stream of dry oxygen is passed. The water liberated is absorbed in a U tube containing Anhydrone. A blank is run on the boat, using 4 g of sodium carbonate.

3.3 Determination of Water in Uranyl Sulfate.¹⁶ The usual methods for the determination of water cannot be employed for the determination of very small amounts of water in uranyl sulfate, because the last traces of water removed during the dehydration of $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ are bound zeolitically and are therefore very difficult to eliminate without decomposition of the salt.

A procedure has been developed for the determination of traces of water which depends on the complete thermal decomposition of the salt and the evolution of hydrogen by sodium metal from the sulfuric acid formed in the process. Thus the method is direct and does not rely on small differences in weight.

(a) Apparatus. The apparatus is shown in Fig. 6.2. The silica decomposition tube is $\frac{1}{2}$ in. in diameter and has two side arms attached to the apparatus by means of a graded silica-pyrex seal and ground joint.

(b) Procedure.¹⁶ The decomposition tube is evacuated and thoroughly flamed, and dry air is allowed to enter from the main system. Small pieces of freshly cut sodium metal are introduced into one of the side tubes of the silica decomposition tube. Into the other side tube is introduced a small platinum boat containing a weighed portion of uranyl sulfate. This operation is performed as quickly as possible. (It has been found, under actual experimental conditions, that the absorption of moisture by uranyl sulfate from the air of the laboratory is less than 0.1 mg in 5 min.) Finally, about half a gram of fine copper wire is introduced in the form of a coil. The decomposition tube is then thoroughly evacuated and isolated from the pumping system. The side tube containing sodium is cooled in liquid air, and the uranyl sulfate is then decomposed by heating, gently at first to avoid decrepitation, and finally with an oxygen-coal-gas flame. Water liberated

in the decomposition, sulfur dioxide, and sulfur trioxide are condensed in the side tube containing sodium. The liberated oxygen is then removed by strongly heating the copper wire. This process usually requires about an hour. The tube is allowed to cool; then the side tube containing sodium is allowed to warm up. The sodium reacts with the acid formed, and hydrogen is liberated. After the pressure has ceased to increase, as noted by the mercury manometer, the side tube is again cooled in liquid air, and the whole operation of cooling

MAIN APPARATUS, PUMPS, AIR INLET, ETC.

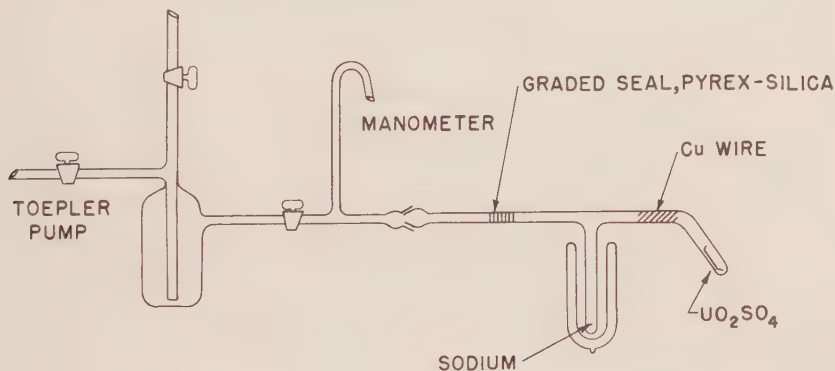


Fig. 6.2 — Apparatus for the determination of water in uranyl sulfate.

and warming up is repeated several times, until the pressure in the system stops increasing. The side tube is cooled again, and the residual, incondensable hydrogen gas is removed through a liquid-air trap by means of the Toepler pump. The hydrogen is then collected and analyzed in a Bone and Wheeler apparatus,²⁷ with an attachment for burning the hydrogen.

It was found that this method gave reproducible results for the amount of water in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and that in all cases the gas was pure hydrogen. As a final precaution the gas samples were treated with alkaline pyrogallol solution; in no instance was any change in volume observed after this treatment.

The quantities of salt used were normally about 0.7 g, and the evolved hydrogen, at room temperature and pressure, was measured with a precision of 0.2 ml. The over-all precision is 3 per cent.

3.4 Determination of Water in Ethereal Solutions.¹⁷ The volumetric method developed by Fischer²⁸ is rapid and specific for water.

The method involves the titration of a methanol suspension or solution of the sample with a reagent composed of iodine and sulfur dioxide dissolved in pyridine and methyl alcohol. The chemistry of the Fischer reagent has been studied in considerable detail by Smith, Bryant, and Mitchell,²⁴ who have also shown it to be specific for water, except for certain metal oxides and carbonyl compounds.

The following method is an application of the method of McKinney and Hall.²⁸ The reagents were stored in all-glass automatic buret systems and were protected from atmospheric moisture by calcium chloride tubes. The reservoir containing the Fischer reagent was enclosed in a light-tight box to prevent deterioration by the action of sunlight. The samples were titrated in 125-ml (standard taper 19/24) glass-stoppered Erlenmeyer flasks, as shown in Fig. 6.3, which had been dried in an oven at 110°C.

Procedure.¹⁷ The water content of the sample is determined by placing 25 ml of the anhydrous solvent methanol (1 liter of methanol is refluxed with 5 to 10 g of magnesium for 3 to 4 hr and then distilled) in a dry Erlenmeyer flask (see Fig. 6.3) and then introducing the measured sample. The Fischer reagent (commercially available from Eimer & Amend) is added until the brown iodine color appears. The solution is then back-titrated with the standard water solution to the electrometric end point. (The standard water solution is prepared by adding sufficient distilled water to dry methanol to give a solution containing approximately 5 mg of water per milliliter.) The shadow on the fluorescent screen, or the "eye," is set at its maximum opening when the electrodes are in the solution containing an excess of the reagent. The eye closes at the end point when the excess reagent is titrated with a standard water solution. There is a slight lag in the closing of the eye which is characteristic of the reaction and takes 2 to 3 sec. Upon approaching the end point, therefore, the rate of adding the standard water solution is reduced. During the titration the contents of the flask are agitated by means of a mechanical stirrer. The moisture content of the sample is calculated from the data as follows:

$$\text{Milligrams of water} = [(KF)(R) - (B_1)(B_t)]F$$

where F is the number of milligrams of water per milliliter of standard solution of water in methanol; KF is the number of milliliters of Fischer reagent; R is the number of milliliters of standard water solution per milliliter of Fischer reagent; B_1 is the blank correction, in milliliters, for the dry solvent methanol of standard solution of water in methanol; and B_t is the back-titration in milliliters of standard solution of water in methanol.

The blank correction for dry methanol, B_1 , and the volume ratio, R , are checked daily. The strength of the standard water-methanol solution, F , is checked weekly by titration against a weighed amount of distilled water.

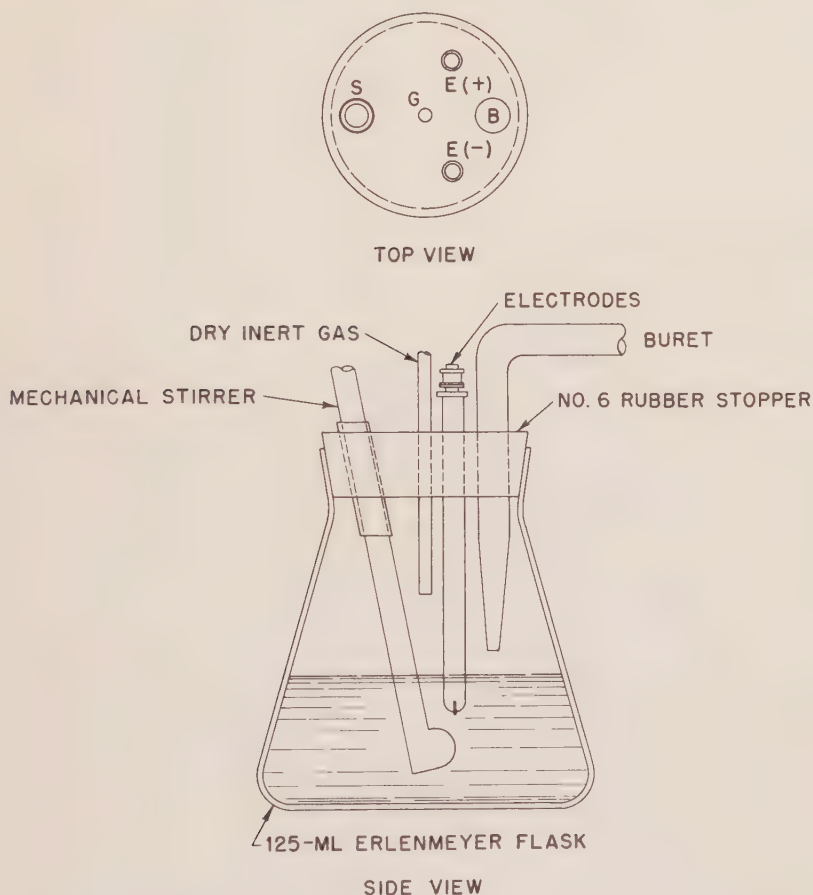


Fig. 6.3 — Titration assembly for the determination of water in ethereal solutions.

4. OXYGEN

Determination of Combined Oxygen in Thorium Metal. Procedure.¹⁸ The sample is cleaned by filing or scraping. A 1.0- to 1.5-g sample of metal is treated with 300 ml of 6N HCl free of dissolved oxygen [bubble nitrogen through HCl (1 to 1) for 5 to 10 min, using a bubble disperser]. The sample is boiled gently for at least 4 hr on a hot

plate. If the solution is faintly yellow, boiling is continued until the yellow color disappears. More 6N HCl is added as needed to keep the volume approximately constant. The sample is cooled, filtered through a Whatman No. 42 filter paper, and washed with dilute HCl (1 to 10). The precipitate is ignited and weighed.

The results on pure metal are comparable to those obtained by vacuum-fusion methods. The method applies only to pure metal samples having no silica or other acid-insoluble material except thorium oxide.

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Chapter 7

CHLORINE, BROMINE, AND IODINE

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Because of their close relation the three halogens—chlorine, bromine, and iodine—are discussed together in this chapter. The rather specialized analytical chemistry of fluorine, the first element of Group VII, is discussed in Chap. 5. Element 85 will not concern the analytical chemist until it has been isolated in amounts detectable by chemical means. Its known isotopes are radioactive, with short half lives, so that it can be determined by the physical methods used in radiochemical analysis.

The wide occurrence of chloride has made its determination important in the analysis of materials for use on the Project. The importance of halides in the study of the basic chemistry of uranium and plutonium has required many analyses for the halogens. The methods described in this chapter were in some cases the result of considerable research; in other cases suitable methods were devised by modifying those in published literature.

1. METHODS OF SOLUTION

Nitric acid is usually employed in dissolving metal and oxide samples. Precautions must be taken against the loss of halogen by volatilization. The uranium halides are very hygroscopic, reacting with water to liberate the hydrogen halide in the case of the bromides and chlorides and to liberate hydrogen iodide or free iodine in the case of the iodides. Dry-box technique is required for the accurate weighing of these samples.

2. METHODS OF DETERMINATION

The gravimetric determination of silver halide has been widely used on the Project. In the range of 100 to 200 mg of chloride, bro-

mide, or iodide the method is employed wherever a high degree of accuracy is required. It has been found to be somewhat more time-consuming than the slightly less accurate volumetric procedures.

The volumetric methods employing silver have been widely used, since they are convenient and accurate enough for most purposes. A special potentiometric modification has been found to be applicable to the determination of very small amounts of chloride and bromide. An electrometric titration using silver nitrate as titrant affords a rapid and accurate means of determining chloride. The Volhard titration has found application in the Project work for the analysis of uranium chlorides, and it was also applied, with slight modifications, to the analysis of bromides and iodides.

The Votocek mercuric nitrate titration for chloride, described later in this chapter, is less complicated than the Volhard method and has been found more accurate in the absence of interfering elements. For large amounts of chloride its accuracy has been found comparable to the gravimetric silver halide determination.

The titration of iodine with sodium thiosulfate is a precise volumetric method with a sensitive end point. It is useful, not only for the determination of iodine, but also for the indirect determination of many other elements. Two methods utilizing this titration are described: one for the determination of very small amounts of iodine, and another for the determination of iodide in mixed uranium halides.

Nephelometric and turbidimetric methods are the most rapid tests for small amounts of halide. They are not highly accurate, but they have been found useful for the determination of traces of halide in uranium and plutonium metals and oxides.

The o-tolidine test was the most sensitive test used for chlorine. Of the two procedures described in this chapter, the micro diffusion method has been found the most satisfactory.

The direct colorimetric test for iodine, in which the element is determined in a chloroform solution, has been found to give very precise results.

The range of the methods employed is given in Table 7.1.

2.1 Gravimetric Method. Determination of Silver Halide. The precipitation of halides,¹ either singly or as "total halogen," with silver nitrate has been frequently applied to the analysis of solutions containing no cyanide, thiocyanate, or other ions precipitable with silver.²⁻⁵ Quadrivalent uranium interferes by reducing silver ion to the metal. In the case of a chloride analysis, uranium(IV) is oxidized to uranyl ion with hydrogen peroxide.^{2,3} This procedure with uranium bromides and iodides may lead to the loss of volatile halogen unless precautions are taken. Another procedure for the elimination of in-

interference by quadrivalent uranium is to precipitate the element as $\text{U}(\text{OH})_4$ with ammonium hydroxide, filter, wash with dilute ammonium hydroxide, acidify the filtrate with dilute nitric acid, and proceed with the determination.

Two standard methods have been used to determine mixtures of two halides. One method used for the analysis of mixed uranium halides consisted in weighing the mixed silver halides, heating in dry chlorine at 400°C to convert all silver to the chloride, and then reweighing.^{1,6} The method of Bekk⁷ was used for the determination of chloride and bromide in mixed uranium halides. The procedure is given below.

Table 7.1 — Range of Methods for Determination of Chlorine, Bromine, and Iodine

Method	Range
Gravimetric	100–300 mg Cl, Br, or I
Volumetric:	
Votocek, 0.1N to 1N Hg^{++}	1–1,000 mg Cl
Volhard	1–100 mg Cl
Micropotentiometric	2–100 γ Cl or Br
Micro thiosulfate	3–800 γ I
Nephelometric	1–20 γ Cl, Br, or I
Colorimetric:	
o-Tolidine	0.1–2.5 γ Cl
I_2 in chloroform	0.5–5 mg I

Procedure.⁸ Two equal aliquots of a sample containing about 0.1 g of halide are taken, the uranium is removed by ammonium hydroxide precipitation, and the halides in both aliquots are precipitated with AgNO_3 . The precipitate from one aliquot is washed, dried at 120°C , and weighed. The precipitate from the other aliquot is washed with dilute HNO_3 to remove excess AgNO_3 . It is then dissolved by heating at 95°C for 30 min in a solution of 2 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 30 ml of H_2SO_4 . Air is blown through the solution for the last 10 min to remove all the liberated chlorine and bromine. The solution is then allowed to cool and is cautiously diluted to about 200 ml; the silver is precipitated with a slight excess of 0.1N KBr. The weight of the AgBr is determined in the usual manner, and the chloride and bromide content of the sample can be calculated from the difference in weight of the precipitates obtained from the two aliquots.

The gravimetric silver halide procedure should give results accurate within 0.1 per cent in the absence of interfering ions. When the method is applied to mixtures of two halides, as in the procedures outlined above, careful work should give an accuracy of 0.2 per cent.

2.2 Volumetric Methods. (a) Potentiometric Titration of Chloride and Bromide. The progress of a titration of chloride or bromide with silver nitrate may be followed by measuring the potential of a silver-silver halide electrode.⁹ A large change of potential of this electrode takes place for a small volume of silver solution added at the end point. The method has been found applicable to quantities too small for the use of chemical indicators.¹⁰ The following procedure is described by Wolf¹¹ for the analysis of small samples of plutonium

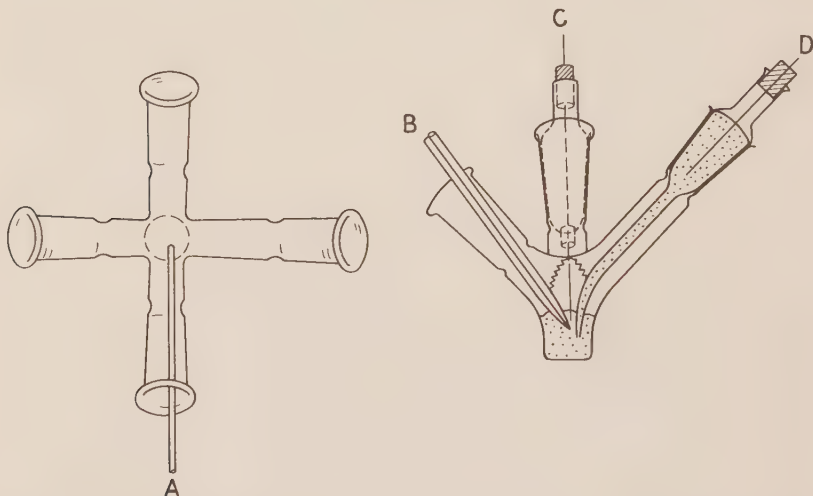


Fig. 7.1—Apparatus for the potentiometric titration of chloride or bromide in 1 ml volume. A, stirrer; B, buret; C, indicator electrode; D, reference electrode.

chlorides and bromides. Other ions forming insoluble salts with silver, as well as reducing agents capable of reducing silver to the metal, will interfere. The procedure was unsuccessful with iodide because the time required for the electrode to reach equilibrium was too great. The method is accurate within 1 or 2 γ in the range of 10 to 100 γ of chloride or bromide.

The titration apparatus shown in Fig. 7.1 accommodates up to 2 ml of solution. The reference electrode, a platinum wire immersed in saturated potassium nitrate, is connected to the solution through a sealed-in asbestos capillary. The silver electrode is a No. 16 B & S silver wire held in place by rubber insulators. Stirring is provided by a glass rod attached to a magnetic vibrator. A calibrated Kirk microburet is used for the standard silver nitrate, and the potential is measured with any potentiometer sensitive to 1 mv.

Procedure. Before a series of titrations the silver electrode is cleaned by immersing in 8N HNO_3 for 2 to 3 min.

A 1-ml aliquot of the sample solution in 0.3N to 0.4N H_2SO_4 is transferred to the titration apparatus. The electrodes, thread stirrer, and microburet are inserted as shown in Fig. 7.1. A preliminary titration is made using fairly large increments of standard 0.5N AgNO_3 . With a second sample a precise titration is performed by using increments near the end point small enough for the accuracy

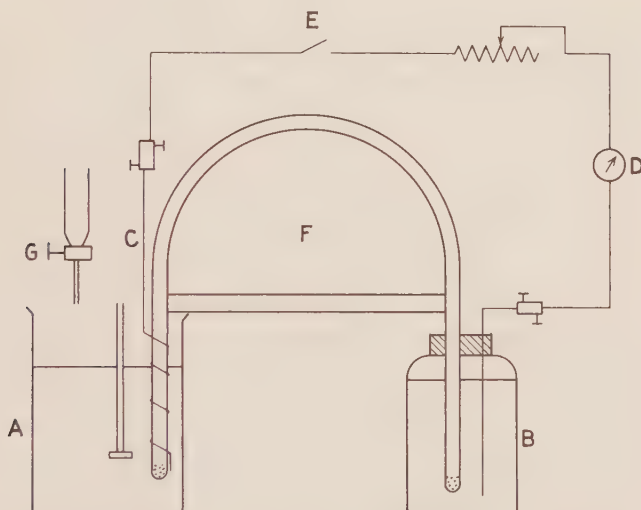


Fig. 7.2—Apparatus for the electrometric determination of chlorides. A, titration vessel; B, reference half cell; C, silver-wire electrode; D, galvanometer; E, switch; F, salt bridge; G, titration buret.

desired. The solution should be kept out of strong light, particularly when bromide is being determined. The electrode is not reversible, but an arbitrary wait of 2 min before each potential reading will yield results consistent enough for a good titration curve.

(b) **Electrometric Titration of Chloride.** Another electrotitration method for chloride using silver nitrate as titrant is the electrometric one in which the end point is determined by the current flow between two silver-wire electrodes, one of which is immersed in the sample, the other in a saturated silver chloride solution. At the end point the current is zero.

This method has provided a rapid means of determining chloride in impure uranium tetrachloride with an accuracy of ± 0.2 per cent.¹⁴

The apparatus is shown in Fig. 7.2. The reference is a silver-silver chloride (saturated) half cell, consisting of a silver wire dipping into a mixture of the following solutions: 25.0 ml of 0.1N NaCl, 25.05 ml of 0.1N AgNO_3 , 10.0 ml of 1.0N HNO_3 , and 40 ml of H_2O . The whole mixture is contained in an amber glass bottle, which is closed with a rubber stopper carrying the silver wire and one limb of a salt bridge.

Any high-resistance galvanometer, such as a Rubicon No. 3402H, is suitable if it has a sensitivity of approximately 12 divisions per microampere and if it reaches equilibrium quickly.

The variable resistance employed is a 10,000-ohm Ayrton shunt.

Procedure for UF_4 .¹⁴ A water solution of the sample containing about 0.15 g of chloride is placed in a 600-ml low-form beaker. H_2O_2 , 3 per cent, is added until the green color disappears; then a few drops are added in excess. A 3-ml quantity of HNO_3 is added, and the solution is diluted to 300 ml. The free limb of the salt bridge F carrying the silver wire C is immersed in the solution in the titration vessel A. The apparatus is so arranged that the liquid levels in the titration vessel and in the reference half cell B are the same. The silver wire is connected in series with the galvanometer, the variable resistance, the tapping key E, and the reference half cell. The galvanometer is adjusted to zero. The sample is stirred and titrated with 0.1N AgNO_3 . The tapping key is momentarily depressed at intervals during the titration, at first after the addition of every few milliliters and, toward the end of the procedure, after every few drops of titrant. The deflection of the galvanometer is noted during the titration, and the buret is read at the point of zero deflection.

A blank is run on the cell and on the reagents used. The cell blank should not be greater than 0.1 to 0.2 ml of 0.1N AgNO_3 .

(c) Volhard Method for Chloride. Quadrivalent uranium interferes with the Volhard method, just as it does in other methods involving precipitation of silver with halides. This interference is minimized by a high concentration of nitric acid, which inhibits the reduction of silver. The use of 3N nitric acid prevents¹⁶ this interference. Bingley¹⁷ has stated that the acidity may be as high as 4N if the solutions are cool. Other methods of chloride determination describe a preliminary treatment with hydrogen peroxide to oxidize uranium(IV) to uranium(VI),¹⁸ or with ammonia to remove uranium by precipitation as $\text{U}(\text{OH})_4$.¹⁹

The "nitrobenzene coating" modification of the Volhard method²⁰ has been discouraged because, when the analyzed samples are subsequently evaporated, considerable explosion hazards may be found to exist if nitrobenzene is present.

The Volhard titration has been used successfully for the analysis of uranium bromides and iodides. The iodide analysis was modified so that ferric alum is added after all the silver iodide has been precipitated to avoid oxidation of iodide by alum.¹ For the determination of "total halide" in mixed uranium halides, the method is said to give poor results.²¹

(d) The Votocek Mercuric Nitrate Titration of Chloride.^{22,23} This method has found some application.^{3,8,24}

Procedure.²⁴ The sample should contain 100 mg, or less, of chloride and 5 ml of HNO_3 . If uranium is present, it should be oxidized by adding H_2O_2 until the solution is yellow. The solution is diluted to 100 to 150 ml, and 1 ml of saturated sodium nitroprusside, freshly prepared, is added. The sample is titrated with 0.1N $\text{Hg}(\text{NO}_3)_2$ to a permanent turbidity. A blank is run on the reagents to the same turbidity, and the volume used for the blank is subtracted from the volume used for the sample. The $\text{Hg}(\text{NO}_3)_2$ solution may be standardized against NaCl or HCl by using the same procedure. If the end point is overrun, a known amount of HCl may be added and the titration continued.

(e) Determination of Iodide by Titration with Sodium Thiosulfate.²⁵ This method has also found some application.

The distillation technique is a micro method suitable for samples in the 100- γ iodine-content range. A tendency for low results is noted with quantities of iodine greater than 100 γ and for high results with smaller amounts. The lowest value obtained in a series of 31 standards containing 50 to 800 γ of iodide was -3.5 per cent on a 400- γ sample, and the highest value was +4.8 per cent on a 50- γ sample.

The extraction technique of Swift,²⁷ using carbon tetrachloride, was modified by using fluoride to prevent further action by entrained ferric alum while the iodine⁸ is being titrated.

Distillation Procedure.²⁶ To the distillation cell, shown in Fig. 7.3, are added 1 ml of sample solution, 4 drops of 0.1N KIO_3 , and 2 drops of 1N H_2SO_4 , or 1 ml of sample, 0.5 ml of 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$, and 0.5 ml of 1N H_2SO_4 . Dichromate is used if other reducing agents are present. In the absorption cell is placed 1 ml of 20 per cent KI solution. The glass beads in the exit tube are wet with the same solution. All the ground-glass joints are wet with dilute H_2SO_4 to prevent leaks. Nitrogen, freed of oxygen by passing over hot copper, is swept through the cell for 10 min. The reaction cell is then warmed gently with a low flame for 5 min more, with nitrogen still passing through the cell.

The absorption cell is opened, a drop of 1N H_2SO_4 is added, and the glass beads are washed down with a few drops of water. The nitrogen is allowed to continue bubbling to provide stirring. The iodine is

titrated with 0.05N $\text{Na}_2\text{S}_2\text{O}_3$, using a microburet, and a starch indicator is added near the end point.

Extraction Procedure.⁸ An aliquot containing 50 to 70 mg of iodine is pipetted into a separatory funnel, and sufficient HCl or H_2SO_4 is added to make the sample 6N in acid. Ten milliliters of 50 per cent ferric alum solution and 25 ml of carbon tetrachloride are then added,

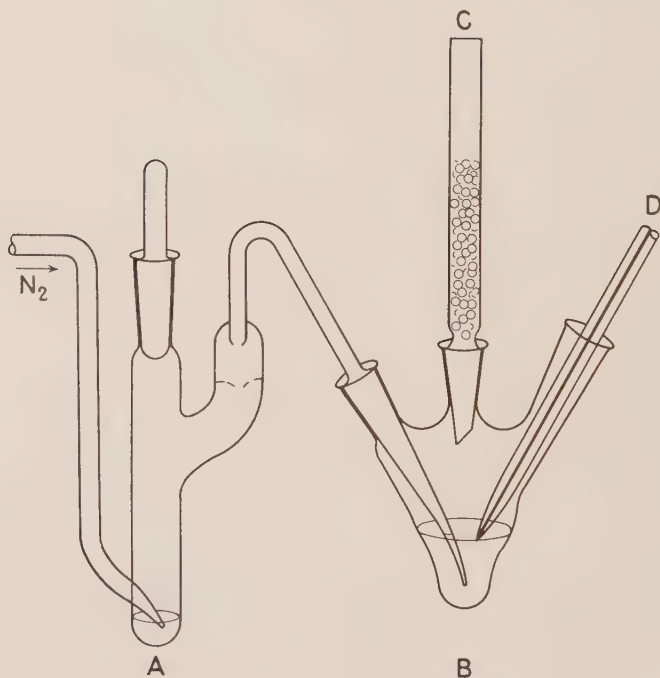


Fig. 7.3—Nitrogen-swept cell for the microvolumetric determination of iodide.²⁷ A, distillation cell; B, cell for absorption and titration of iodine; C, gas escape vent; D, drop-scale buret.

and the mixture is shaken occasionally for 5 min. The layers are then allowed to separate, and the carbon tetrachloride–iodine layer is drawn off into an iodine flask. The stem of the funnel is rinsed with distilled water, and the rinsings are caught in the iodine flask. The extraction is repeated with 20-ml portions of carbon tetrachloride until no color appears in the carbon tetrachloride layer. The stem of the funnel is rinsed with water after each extraction. To the combined carbon tetrachloride layers and rinsings in the iodine flask are added 1 ml of 6N H_2SO_4 and 5 ml of 20 per cent ammonium bifluoride

solution. (The fluoride is added to prevent further action by any ferrous ion that may have become entrained in the extracts.) A 1-ml sample of starch indicator solution is then added, and the sample is titrated with 0.02N $\text{Na}_2\text{S}_2\text{O}_3$. Near the end of the titration the flask should be stoppered occasionally and shaken vigorously.

2.3 Nephelometric and Turbidimetric Methods. The precipitates formed when silver nitrate is added to dilute acid solutions containing small quantities of chloride, bromide, or iodide are suitable for nephelometric or turbidimetric determinations.²⁸ These methods are simple, fairly accurate, and quite sensitive.²⁹⁻³⁴ Since the methods are extremely sensitive, the hazard of contamination from dust and fumes is very great, and careful technique is necessary if good results are to be obtained.

Other ions forming insoluble silver salts, such as cyanide and thiocyanate, and ions that reduce silver to the metal, such as quadrivalent uranium, must be absent. All colored ions that would normally interfere in ordinary colorimetric determinations are corrected for by taking another aliquot of the same solution and adding to it all the reagents except the silver nitrate. This solution and the precipitated solution are both measured against distilled water blanks containing all the reagents.

The nephelometric or turbidimetric determination may be carried out directly on a solution of the material being analyzed, or the hydrogen halide may be separated by distillation and the test made on the distillate.

The turbidity of the silver halide suspension may be compared with standards visually,³³ compared with standards in Nessler tubes,³¹ or measured with a nephelometer^{30,34} or a spectrophotometer.³⁰

A turbidimetric procedure based on published methods and utilizing a Coleman model 11 spectrophotometer has been adapted to the trace analysis of chloride in water.²⁹

(a) Distillation of Hydrogen Halides. A method has been used³³ for the analysis of uranium metal and uranium oxides in which the sample is dissolved in 85 per cent phosphoric acid in a still. The phosphoric acid solution is then heated in a phosphoric acid bath at 150°C, and the hydrogen halide is distilled off and caught in 25 ml of 5 per cent silver nitrate solution. The turbidity produced by the sample is visually compared with that of the standards carried through all steps of the operation.

In a procedure employed for the trace determination of chloride in uranium³⁰ the sample is dissolved in nitric acid, and the hydrogen chloride is separated by steam distillation. The opalescence produced by the addition of silver nitrate to the distillate is measured with a nephelometer.

The range with a nephelometer is about 1 to 20 γ of chloride in a final volume of 50 ml,^{30,34} with an accuracy of 1 to 2 γ . In a procedure using a Coleman model 11 spectrophotometer at 350 m μ with 19-mm cylindrical cuvettes, a range of 5 to 100 γ was obtained.²⁹

(b) Direct Nephelometric Determination of Chloride. A direct method was developed for the nephelometric determination of chloride in uranium and magnesium metals.³⁰ In this procedure the sample of uranium or magnesium is dissolved in nitric acid in an apparatus designed to prevent the loss of chloride by spattering or volatilization. The apparatus consists of a 25-ml Erlenmeyer flask attached to a standard-taper 15/35 ground-glass interjoint. The upper portion is a 13-cm glass column. This column is filled with 3- to 5-mm glass beads supported by a constriction in the tube and by several glass helices and is closed at the top with an inverted test tube.

Procedure for Uranium Metal.³⁰ A sample of 0.8 to 1.5 g of uranium is weighed to the nearest 0.01 g and cleaned in redistilled HNO₃. A light cleaning to remove superficial oxide causes only a negligible error. The sample is transferred to the 25-ml Erlenmeyer flask of the chloride apparatus, and 5 ml of redistilled HNO₃ is added. (This amount of acid provides a 2-ml excess.) The tube containing the glass beads previously moistened with distilled water is connected to the flask, and the sample is dissolved by heating on a low-temperature hot plate covered with an asbestos pad. The solution is then allowed to cool and is transferred to a 100-ml glass-stoppered graduate, the apparatus being thoroughly washed with distilled water. The sample solution and washings are made up to a volume of 60 ml with distilled water, 10 ml of 0.01N AgNO₃ is added, and the solution is mixed thoroughly and allowed to stand in the dark for 1 hr. The opalescence of the sample is then compared with the opalescence of a standard in a nephelometer of the design of Richards and Wells.^{35,36} The optimum amount for the standard was found to be 7 γ of chloride. Calibration curves were obtained by adding the calculated amount of chloride to 2 ml of redistilled HNO₃, diluting to 60 ml, and proceeding as with a regular sample.

A blank is run for each series of samples on 2 ml of redistilled HNO₃. The blank should contain less than 1 γ of chloride. Variations in the uranium content of the samples from 0.8 to 1.6 g produced no difference in readings. It was also observed that no error was involved in reading such samples against a standard to which no uranium was added.

The accuracy of the method is approximately 4 per cent in the range of 3 to 15 γ of chloride.

2.4 Colorimetric Methods. (a) Direct Determination of Iodine. The direct colorimetric evaluation of iodine in chloroform or carbon

tetrachloride extracts based on the work of McClendon³⁷ has been employed by Jensen.³⁸ This method is accurate to ± 5 per cent on samples containing 0.5 to 5.0 mg of iodine or iodide. Reducing agents, including large amounts of bromide or chloride, interfere. Selection of an oxidizing agent other than KIO_3 , for example, $\text{K}_2\text{Cr}_2\text{O}_7$, for the oxidation of iodide is recommended in some cases to avoid oxidation of ions such as chloride.

Procedure for Free Iodine.³⁸ A solution of the sample is shaken with 10-ml portions of chloroform until the extracts are colorless. The combined extracts are diluted to 50 ml with chloroform, and the optical density at $510 \text{ m}\mu$ is measured with a spectrophotometer against a pure chloroform blank. Beer's law is obeyed up to 5 mg.

Procedure for Iodide. To the sample solution in a separatory funnel is added 50 mg of KIO_3 crystals. After solution 10 ml of chloroform and 1 ml of HNO_3 are added. The extraction and colorimetric determination are performed as above.

(b) Orthotolidine Micro Diffusion Method for Chloride. Certain organic bases, including *o*-tolidine, $[\text{NH}_2(\text{CH}_3)\text{C}_6\text{H}_3]_2$, are oxidized to yellow compounds of unknown composition by strong oxidizing agents, such as free chlorine.³⁹ Chloride can be oxidized to chlorine by permanganate, distilled into a potassium hydroxide solution, and tested with the reagent. By using the micro diffusion technique of Conway⁴⁰ the method may be applied to small quantities of chloride. The extension of the technique to very small amounts of chloride has been studied by Watters.⁴¹⁻⁴³

Nitrite and bromide interfere, since nitrogen dioxide and bromine also oxidize *o*-tolidine. Iodine interferes only because of its own color. These interferences are prevented by a special procedure, which includes a preliminary dichromate oxidation.

The procedure is applicable to the determination of 0.1 to 2.5 γ of chlorine by using a final volume of 1 ml, but it can be used for larger amounts by using a larger volume of *o*-tolidine reagent. Beer's law is followed in this range. A precision of about 0.03 γ and an accuracy of about 10 per cent have been obtained in the absence of bromide. The procedure for use when bromide is present is slightly less precise.⁴⁴ Because of the small amounts of chlorine determined, extreme care must be used to prevent contamination from the dust or acid fumes so commonly found in laboratories.

(c) Fabrication of a Micro Diffusion Cell.⁴³ An 11-mm section is cut from pyrex tubing of 22 mm outside diameter; a 7-mm section is cut from pyrex tubing of 10 mm outside diameter; and a glass square 25 mm on an edge is cut from a pyrex plate 1 to 2 mm thick. One end of the smaller tubing is fire-polished with an oxygen hand torch and is placed, polished end down, on an asbestos disk 4 mm in height and

about 16 mm in diameter. The larger section is placed over the whole, and then the glass square is placed on top. A full luminous flame is obtained. When a dull red color is observed, pressure is applied with a flat graphite surface and repeated until a seal is obtained between each cylinder and the glass square. (The corners of the glass square will have fallen, but this is actually an advantage in handling the cells during use.) The sealed parts are quickly transferred to an asbestos-covered gauze above a full Meker flame and covered with a large cone of asbestos paper. After 2 hr the flame is reduced, and in another half hour it is removed. The top edge of the outer cell is polished on a glass plate with emery dust and water. The covers are readily prepared by cutting microscope slides or spectrograph plates into squares 24 mm on an edge.

Procedure with Bromide Absent.⁴³ The entire bottom of the outer chamber of the clean diffusion cell is wet with 25 μ liters of water by brushing with a small glass rod. The soluble chloride sample is transferred to the outer chamber. To the central chamber is added 50 μ liters of 0.1N KOH (any trace of reducing agent is destroyed by adding chlorine water drop by drop until barely measurable coloration appears when 10 ml of the solution is treated with 2 ml of *o*-tolidine reagent) without wetting the upper portion of the wall. The top edge of the outer cell is barely wet with a glass rod covered with a thin film of cover-glass fixative (H_2SO_4). To the sample in the outer cell is added approximately 150 μ liters of acidic permanganate solution freshly prepared by mixing 4 volumes of 9N H_2SO_4 with 3 volumes of 6.5 per cent KMnO_4 (recrystallized). The cover glass is quickly put in place, care being taken that the seal is complete. The reagents are best added from a micropipet, with the tip touching the outer side wall but avoiding other contacts with the walls. To prevent spattering, the last trace of the solution is not ejected from the pipet.

The solutions are mixed by gently rotating the cell. The cell is left covered with a cardboard-box cover for 3 hr at room temperature or for 50 min in a 40°C incubator.

Approximately 0.8 ml of dilute *o*-tolidine reagent (1 g of *o*-tolidine is titrated with 5 ml of 3N HCl and dissolved by adding 150 ml of water; as needed, 5 ml of this solution is diluted to 100 ml with water that has been treated with 1 ml of chlorine water and then boiled) is transferred to a small crucible. Most of this reagent is withdrawn into a very fine-tipped medicine dropper fitted with a large bulb. Without releasing the bulb the contents of the inner cell are withdrawn into the same dropper, and the solutions are mixed by allowing small air bubbles to be drawn in. The solution is transferred to a 1-ml volumetric flask. The cell and dropper are rinsed with the remainder of

the reagent in two or three portions, combining the washings with the solution. The solution is diluted to 1 ml with additional reagent; after mixing, it is transferred to a cuvette. The standard 4-ml 1-cm Beckman cuvette may be used, with the adapter described in Chap. 24, "Photometric Methods." The optical density is measured at 440 m μ and compared with a curve obtained by using known quantities of chloride. Beer's law is obeyed in the range of 0 to 2.5 γ of chlorine.

Procedure with Bromine Present.⁴³ For samples containing bromine the procedure outlined above is preceded by a similar diffusion, using 150 μ liters of acidic dichromate solution (9 g of recrystallized $K_2Cr_2O_7$ and 40 ml of H_2SO_4 in 60 ml of redistilled H_2O ; if a precipitate forms on cooling, the solution is decanted, and 1 ml of H_2O is added) instead of permanganate. After standing 4 hr at 25°C, or 50 min at 40°C, the contents of the inner chamber are removed. The inner chamber is rinsed with 0.1N KOH until free of bromine; then the procedure for chlorine is carried out as above. The washing can be tested for bromine by adding it to a little *o*-tolidine reagent in a crucible.

The cell may be cleaned by rinsing with water, immersing for a few minutes in a dilute solution of hydroxylamine in dilute sulfuric acid, rinsing, immersing in a warm chromic acid cleaning solution, and rinsing several times with distilled water. Most of the water is shaken off, and the cell is dried (inverted) in a dust-free oven.

(d) Orthotolidine Determination of Chloride with Nitrogen-swept Cell. Another technique for the separation of chlorine for determination by the *o*-tolidine reaction is the nitrogen-swept-cell procedure developed by Watters and Orlemann.^{12,13,15} The sample is dissolved in sulfuric acid. Hydrogen chloride is removed by distillation in a stream of nitrogen, oxidized to free chlorine by passing through a lead dioxide-sulfuric acid mixture, and absorbed in *o*-tolidine reagent. Potassium permanganate cannot be used as an oxidant because it is decomposed by the high temperatures employed. The yellow color of the oxidized *o*-tolidine is then measured as described in the previous method.

Uranium metal, which is not readily soluble in sulfuric acid, has been dissolved by anodic oxidation with a pair of platinum electrodes sealed into a ground-glass male joint fitting the reaction chamber. The anode is a platinum-gauze cylinder, which will hold the sample piece. This procedure has been used satisfactorily and without incident for this determination, but it is not recommended because of the danger of explosion of the hydrogen and oxygen produced in the closed system.

Nitric acid and hydrogen peroxide treatments will dissolve uranium metal, but these methods have proved unsatisfactory because of high

blanks. For these reasons the method is not recommended for uranium metal.

The method is applicable to the determination of 0.1 to 2.5 γ of chlorine. When micro-Nessler tubes prepared from 4-mm pyrex tubing wrapped in dark paper were used, an accuracy of 20 per cent was obtained.

The apparatus is more complicated than that of the micro diffusion method, its operation requires more skill, and constant attention is required. However, the procedure has been found useful for certain samples.

Bromides and nitrites interfere. Bromide gives the same color as an equivalent amount of chloride. Iodide, up to 10 γ , does not interfere at all. Bromide has been removed by preliminary dichromate oxidation, but larger blanks ensued.

The distillation unit is shown in Fig. 7.4. The most important detail is an efficient spray trap above the lead dioxide to prevent entrainment of the oxidizing agent. Tank nitrogen used in the apparatus is purified by passing it first through a wash tower containing a solution of 0.02M potassium permanganate in 0.05M sulfuric acid and then through a wash tower containing 0.01M sodium hydroxide. The chloride is liberated as hydrogen chloride at B, oxidized to chlorine by lead oxide in E, and absorbed in *o*-tolidine reagent at F.¹⁵

Procedure.¹⁵ The apparatus is first thoroughly cleaned by applying suction from a water aspirator at A, while the tip at F is immersed first in cleaning solution and then in several portions of water. Air is then drawn through the apparatus to remove most of the moisture. Next, 0.6 ml of the PbO_2 suspension (2 g of powdered PbO_2 is added to 25 ml of H_2SO_4 and shaken before using; the blanks are better if the reagent is several days old) is introduced by a small pipet into the dissolver, which is tilted so that the drops will fall into the outlet D while gentle suction is applied at F. Approximately 1 ml of H_2SO_4 is introduced into the dissolver, and the ground-glass stopper is sealed with a little H_2SO_4 . Inlet A is connected to the nitrogen source, and the chlorine absorber, containing nearly 1 ml of dilute *o*-tolidine reagent (prepared as described in the previous method), is connected before any pressure is applied. The dissolver and oxidizer are placed in a 250-ml beaker nearly filled with H_2SO_4 heated to 130°C. A uniform temperature is attained by placing the beaker on an electric hot plate connected in series with a variable resistance. After allowing 2 min for the cell to reach the temperature of the bath, the nitrogen pressure is gradually increased until bubbles form at the rate of about two per second. The absorber is immersed in a small beaker of ice water. At 6-min intervals the chlorine absorber is removed

and replaced by a duplicate containing fresh reagent. The *o*-tolidine solution is diluted to 1 ml with additional reagent, and its transmittancy at $440\text{ m}\mu$ is measured with a spectrophotometer. When the chlorine content of successive portions reaches a small constant value (the blank), the chlorine absorber, the nitrogen pressure tube, and

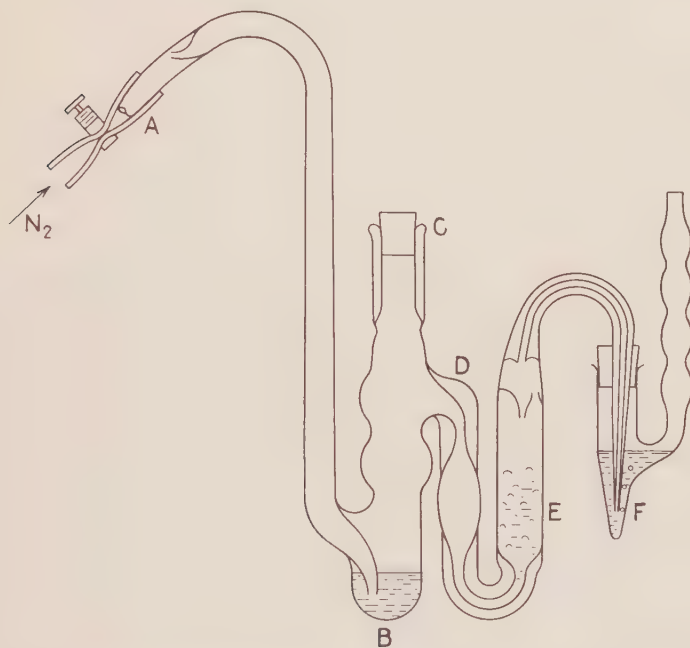


Fig. 7.4—Apparatus for chloride determination modified for electrolytic solution of metal samples. A, nitrogen inlet; B, dissolver; C, electrolysis assembly, made of platinum and glass; D, connection to oxidizer prepared from heavy-walled capillary tubing of 3 mm inside diameter; E, oxidizer containing glass beads; F, chlorine absorber.

then the stopper are removed. The apparatus is removed from the bath. The sample is dropped into the dissolver B, and the stopper is replaced. The apparatus is again immersed in the 130°C bath, and the procedure is carried out as in the blank. The chlorine is quantitatively liberated in 6 min of bubbling.

It is particularly important that the cell be immersed in the bath for 2 min before turning on the nitrogen and that the rate of nitrogen flow be slow at the beginning to avoid loss of chlorine.

Metal samples are dissolved electrolytically by applying about 20 volts direct current at room temperature.

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Chapter 8

SULFUR, SELENIUM, AND TELLURIUM

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The elements of Group VI-B of the periodic table show considerable differences in their chemical and physical properties. The special analytical procedures and techniques for oxygen are discussed in Chap. 27 on "Low-pressure Methods," Chap. 29 on "Other Methods," and Chap. 6 on "Carbon, Hydrogen, and Oxygen." Sulfur is sufficiently different from all other elements so that its separation is relatively simple. Sulfide sulfur was of interest in metals in which it occurred in trace quantities. Selenium and tellurium resemble each other so closely that they are discussed together in this chapter. Because of its radioactive properties, polonium is detected and determined by the physical methods used in radiochemical analysis.

1. SULFUR

1.1 Methods of Solution. Sulfur usually exists as the sulfide both in metal samples and in many of the inorganic compounds examined. Such sulfur is lost if the samples are dissolved in acid before the sulfide is oxidized. In many cases evolution with acid is employed as a means of separation. Fusion with sodium peroxide or with a mixture of sodium carbonate and potassium nitrate converts the sulfur to a soluble sulfate. Solutions of sulfates should not be evaporated to dryness at high temperatures because losses may result.

1.2 Methods of Determination. The conventional gravimetric method, whereby sulfate ion is precipitated with barium ion, was widely used on the Project. The titrimetric methods are satisfactory for relatively large amounts of sulfide. For trace determinations of sulfide the methylene blue colorimetric method is satisfactory; the lead sulfide-stain method is more sensitive but less accurate. The nephelometric barium sulfate method or the colorimetric estimation

with benzidine has also been used. The range of the methods used is given in Table 8.1.

(a) Gravimetric Method. Sulfate is most often determined by precipitation from dilute acid solution as barium sulfate, which can be ignited and weighed. The procedure and the errors involved are adequately discussed in standard works.¹⁻⁴ The method was used extensively on the Manhattan Project for the analysis of various materials.⁵⁻¹¹ Organic materials containing sulfur may be converted to

Table 8.1—Range of Methods for Determination of Sulfur

Method	Range
Gravimetric:	
Barium sulfate	1–200 mg
Titrimetric:	
Benzidine sulfate	0.5–50 mg
Iodine	0.5–50 mg
Silver thiocyanate	0.1–50 mg
Colorimetric:	
Benzidine	70–300 γ
Methylene blue	1–15 γ
Lead sulfide	0.2–10 γ
Nephelometric:	
Barium sulfate	4–300 γ

sulfate in a Parr bomb prior to precipitation. The presence of uranium in the solution presents no special problem. The following procedure has been used for the determination of sulfur in uranium tetrafluoride.

Procedure.¹² A 3-g sample is ground with 3 g of anhydrous sodium carbonate in an agate mortar, and this mixture is placed over a small amount of carbonate in a 25-ml platinum crucible. Two small separate portions of carbonate are used to clean out the mortar and are added to the crucible. The total carbonate used should be 5 g.

The crucible is covered, placed in a muffle furnace, and allowed to sinter overnight at 650°C. The contents are then transferred to a 600-ml beaker, and 250 ml of H₂O and 10 ml of HCl are added. The contents are then stirred and warmed until solution occurs. Any residue is filtered off and is washed thoroughly with hot water.

The sulfate is precipitated in the boiling filtrate, having a volume of 500 ml, with 30 ml of hot barium chloride solution (10 per cent), and the solution is digested on the steam bath overnight. It is then filtered through a fine paper and washed thoroughly with hot water.

Next it is transferred to a tared platinum, porcelain, or silica crucible. The paper is burned off at a low temperature, and the sample is finally ignited at 1000°C to constant weight. A blank is run in the same manner, and the results are corrected accordingly.

(b) Volumetric Methods. The determination of sulfide sulfur in metals and in sulfide-bearing materials was usually made by one of the volumetric methods. The iodometric³ and silver thiocyanate methods, the method based on the reduction of calcium hypochlorite,¹³ and the benzidine sulfate method were employed.

(1) Iodometric Method. The conventional iodometric method,³ as used in the analysis of steel, was employed without modification.¹⁴

In the absence of other reducing substances, sulfide can be determined by titration in a slightly acidic solution with standard iodine or

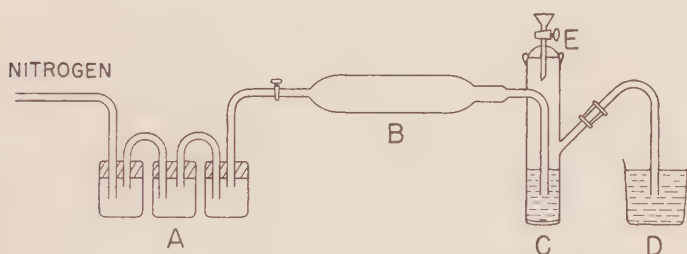


Fig. 8.1—Apparatus for H_2S evolution. A, pyrogallous acid scrubber; B, CoO tube at room temperature; C, reaction chamber; D, $\text{Zn}(\text{NH}_3)_4^{++}$ solution; E, ground-glass stopper.

with potassium iodate solution after the addition of excess iodide.^{3,15,16} Iodate may be used instead of iodine, because in acidic solutions the oxidation of iodide by iodate to iodine is very rapid. Sulfide is separated from interfering ions by distillation as hydrogen sulfide.

The macro procedure outlined by Scott³ was scaled down to the range of 10 to 300 γ by Hubbard,¹⁶ who used 0.003N potassium iodate-potassium iodide solution and milligram samples of metals. The sulfur is reduced to sulfide by fusion with calcium. Standardizations of the procedure with barium sulfate showed a precision of about 2 per cent.

Procedure for Solids.¹⁶ About 1 mg of sample is weighed (micro balance) in a small pyrex-glass capsule, which will just slide down into the reaction chamber (see Fig. 8.1). Fifty milligrams of calcium metal is added, and the mixture is fused over a small gas flame. The capsule containing the fused mass is dropped into the reaction chamber while it is still hot enough to be shattered by contact with the cold water in the bottom of the reaction chamber. The glass stopper is

inserted, and the nitrogen is turned on and allowed to bubble slowly through the pyrogallic acid scrubber, the CoO tube, the reaction chamber, and finally the ammoniacal zinc sulfate solution (200 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 1 liter of H_2O , to which is added 1 liter of NH_4OH). A 15-ml sample of HCl (1 to 1) is made to enter through the funnel at the top of the reaction chamber, the stopcock is closed, and the nitrogen is allowed to continue bubbling for 30 min. The side arm entering

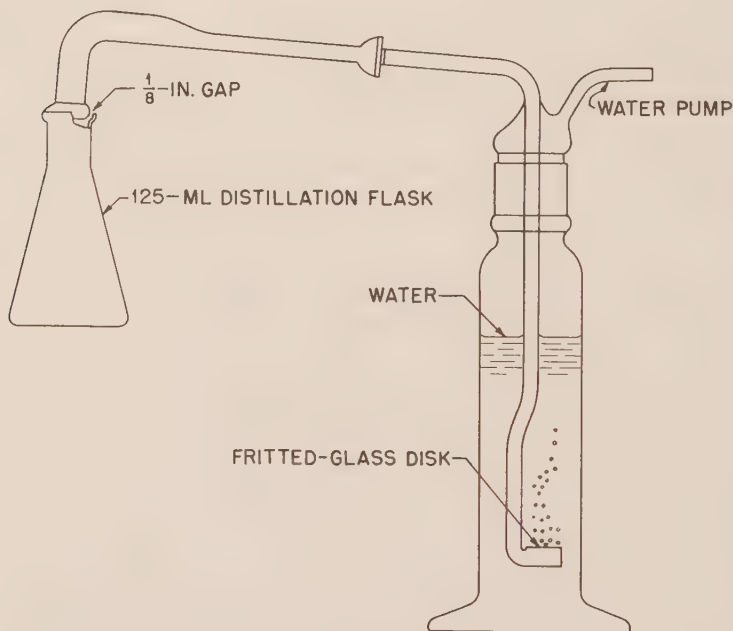


Fig. 8.2—Evaporation apparatus for the removal of nitrate.

the ammoniacal zinc sulfate solution is then disconnected, and the solution is acidified with 20 ml of HCl (1 to 1) and titrated with KIO_3 - KI solution (1.12 g of KIO_3 and 12 g of KI in 1 liter of H_2O) to the starch end point. The KIO_3 - KI is standardized against reagent-grade BaSO_4 , and a blank is run and subtracted from the titer of the sample.

For the determination of sulfate in solution, the method based on the procedure of Luke¹⁷ has been employed.¹³ The sulfate is reduced to sulfide by means of a reducing system composed of hydriodic, hypophosphorous, and hydrochloric acids. The hydrogen sulfide is trapped in an ammoniacal cadmium chloride solution, and the sulfide sulfur is then determined iodometrically.

Procedure for Sulfate Solutions.¹³ If the sample contains nitrate, the nitrate must be removed. A convenient apparatus for the removal of nitrate is shown in Fig. 8.2. The nitrate is removed as follows:

An aliquot of the sample is pipetted into the distillation flask. The solution is evaporated with 5 ml of 70 per cent perchloric acid and is boiled vigorously to drive off all traces of nitrate. An indication of

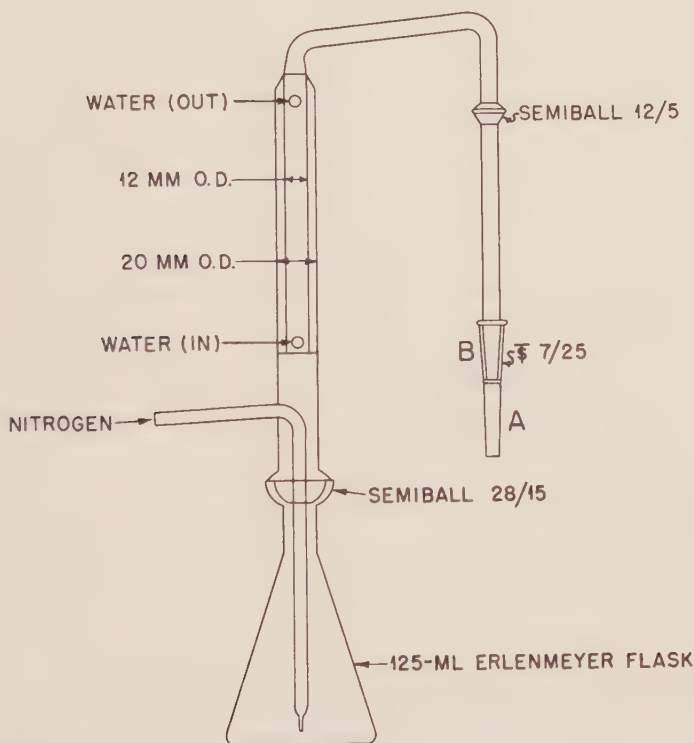


Fig. 8.3—Distillation apparatus for the determination of sulfate sulfur.

sufficiently vigorous boiling is the absence of HClO_4 condensate in the distillation flask. The semiball joint is not closed completely, but is clamped so that a small gap is left between the male and female parts of the joint. The solution is evaporated until the volume is decreased to 1 to 2 ml. This procedure removes the nitrate in one evaporation. The residual perchloric acid will not react explosively with the reducing mixture. The flask is cooled, and the distillation of hydrogen sulfide is made by using the setup shown in Fig. 8.3.

A 50-ml sample of the ammoniacal cadmium chloride solution (10 g of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and 500 ml of NH_4OH diluted to 1 liter) is put in a 250-ml iodine flask, which is placed in position with the end of the delivery tube A touching the bottom of the flask. To the sample in the distillation flask are added a few glass beads and 20 ml of the reducing mixture (160 ml of 47 per cent HI , 160 ml of HCl , and 40 ml of 30 per cent hypophosphorous acid are mixed, boiled for 5 min, cooled, and stored). The flask is immediately connected to the still. The heater is placed in position, and the solution is brought to a rapid boil. When H_2S stops coming over (after approximately 10 min), nitrogen is bubbled through the boiling solution gently for 10 to 15 min.

At the end of the distillation the delivery tube is disconnected at the semiball joint, and the inside of the tube is washed down with a few milliliters of water. The lower part of the delivery tube is disconnected at the standard-taper joint B and is left in the receiver. The heater is removed, and the gas stream is stopped.

A 10-ml sample of HCl is added to the cadmium sulfide solution in the iodine flask, which is stoppered immediately, swirled to mix the contents, and then placed in an ice bath. When the solution is cold, it is removed from the ice bath, and 1 ml of the iodine solution (0.1N I_2 -KI standardized against arsenious oxide in the usual manner) is pipetted into the cup of the iodine flask. The stopper is cautiously loosened so that the iodine is drawn into the flask without allowing any of the H_2S to escape. The iodine is then washed into the flask with small portions of distilled water, care being taken at all times not to remove the stopper completely. The partial vacuum will draw in the wash water without difficulty.

The flask is shaken well so that all the H_2S will react with the iodine. Then the flask is allowed to come to room temperature. The solution is titrated with a 0.01N thiosulfate solution (standardized by carrying 1 ml of a standard Na_2S solution through the procedure), starch indicator is added just before the end point, and the titration is continued until the disappearance of the blue color.

(2) Silver Thiocyanate Method. Another method for the determination of hydrogen sulfide is to absorb the gas in an ammoniacal solution of standard silver nitrate, thus precipitating an equivalent amount of silver sulfide. The silver that remains in solution after removal of the silver sulfide by filtration can be determined by titration with thiocyanate by the Volhard method.^{15,18,19} Since chloride must be absent, sulfuric or perchloric acid is used to liberate the hydrogen sulfide. The adsorption of silver ions by the silver sulfide precipitate is estimated to cause an error of about 1 per cent.¹⁵

The method was developed for the analysis of barium, cerium, and thorium sulfides. Bromley and Lofgren¹⁵ considered it the best meth-

od for the purpose. Complete solution of the sample could not always be attained with cerium sulfide containing a large amount of oxide or with thorium sulfide.

The accuracy of this method was found to be better than 1 per cent when the sample was completely soluble and no carbide was present. The presence of considerable carbide impurity causes an error on account of the precipitation of some silver by acetylene.

Procedure.¹⁸ A 0.2-g sample is weighed into a glass capsule, which is placed in a 125-ml Erlenmeyer flask. This flask is connected by a two-hole rubber stopper and glass tubing to another 125-ml Erlenmeyer flask, which contains a 2- or 3-ml excess of 0.1N AgNO_3 solution, 30 ml of 6N NH_4OH , and about 50 ml of H_2O . Forty milliliters of acid is added through a funnel in the stopper of the first flask by using 2N HClO_4 for ThS_2 , 0.5N HClO_4 for BaS , and 0.3N H_2SO_4 for Ce_2S_3 . The contents of the first flask are boiled, and the boiling is continued for several minutes after the reaction has stopped. The perchloric acid concentration is not allowed to rise above its initial value. At higher concentrations some perchlorate is reduced to chloride, which is then distilled into the receiver as hydrogen chloride and there precipitates some of the silver.

The precipitated silver sulfide is filtered and washed several times with hot water; then 30 ml of HNO_3 and 5 ml of 4 per cent ferric alum indicator solution are added to the filtrate. The filtrate is cooled to room temperature, and the excess silver is titrated with 0.1N KSCN to a pink color.

(3) Calcium Hypochlorite Method. In a method used for the determination of acid-soluble sulfide in metal,²⁰ the sulfur is distilled as hydrogen sulfide and absorbed in an excess of calcium hypochlorite. The sulfur is oxidized to sulfate, and the excess calcium hypochlorite is determined iodometrically. Quantitative results are obtained by determining the titer values of the reagents against known quantities of sulfide.

Procedure.²⁰ The still is assembled as shown in Fig. 8.4, and the weighed sample and 3 ml of H_2O are introduced into flask B. One milliliter of 0.01N calcium hypochlorite²¹ is pipetted into a 25-ml receiving flask, and a little distilled water is added so that the tip of the condenser is below the surface of the solution. Sufficient HCl is added through A to make the solution in B approximately 1N, and the acid is washed down with a little water. The air is connected and adjusted to a moderate rate so that the flow is rapid enough to prevent sucking back when the still cools. The solution in B is heated to incipient boiling. The air stream continues to sweep over the liberated H_2S for 5 min. (The sample must be in solution before starting the 5-min sweep interval. Gentle heating below the boiling point is per-

missible to ensure complete solution. The air stream is kept flowing throughout the entire operation.) The tip is disconnected, the inside is washed with a small quantity of water, and the washings are collected in the receiving flask. Two milliliters of 0.1N KI and 2 drops of H_2SO_4 are added. After 3 to 4 min the solution is titrated with a 0.01N sodium thiosulfate solution, with 2 drops of starch indicator added just before the end point.

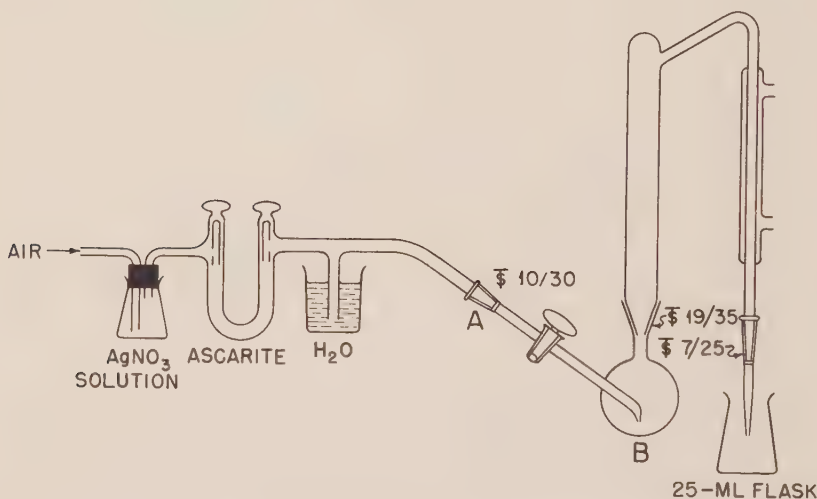


Fig. 8.4—Distillation apparatus for the determination of acid-soluble sulfide sulfur.

The blank is determined by running through the distillation procedure without added sulfide. The blank is positive and constant; it is apparently caused by the destruction of a small quantity of hypochlorite during the distillation.

(4) Benzidine Sulfate Method. Benzidine dihydrochloride forms an insoluble precipitate, $\text{NH}_2(\text{C}_6\text{H}_4)_2 \text{NH}_2 \cdot \text{H}_2\text{SO}_4$, with sulfate ion in slightly acidic solution. After filtration this precipitate is hydrolyzed with a known volume of standard alkali, and the excess alkali is back-titrated with standard acid by using phenolphthalein as the indicator.²²⁻²⁴ Moderate amounts of other acids and salts do not interfere. For example, 200 mg of uranyl nitrate, 8 mg of aluminum nitrate, 4.5 mg of ferric nitrate, and 20 mg of mercuric nitrate caused no interference. In the range of 40 to 100 mg of sulfate the accuracy is 2 per cent.²² The procedure that has been used is that of Raschig,²⁴ as modified by Goldsmith²² for use with uranyl nitrate solutions.

Procedure.²² An aliquot of the solution to be analyzed is taken which contains less than 0.1 g of sulfate ion. (Since sulfate ion will not be quantitatively precipitated if present in amounts exceeding 0.1 g, the validity of the analysis may be checked by taking two aliquots, one twice the volume of the other.) The aliquot is diluted to 50 ml, and the pH is adjusted to a value between 2 and 3. With vigorous stirring 40 ml of the benzidine dihydrochloride solution (8 g of benzidine dihydrochloride is mixed with 20 ml of H_2O , 5 ml of HCl is then added, and the mixture is diluted to 1 liter with H_2O) is added. The precipitate is allowed to settle for 15 min, after which it is filtered by suction through a Whatman No. 42 filter paper supported by a platinum cone. The precipitate is washed four or five times with 5-ml portions of cold water, the precipitate being dried after each washing. The precipitate and paper are transferred to a 500-ml Erlenmeyer flask, 100 ml of H_2O is added, and the stoppered flask is shaken until the filter paper is thoroughly macerated. The sides of the stopper and flask are washed down with cold water, and 2 drops of phenolphthalein solution are added. A 25-ml sample of the standard base (0.1N NaOH) is then added, and the solution is warmed to 50°C . The contents of the flask are swirled thoroughly, and the solution is back-titrated with the 0.05N HCl .

(c) **Colorimetric Methods.** Modifications of several of the common methods for the colorimetric determination of sulfur have been employed. They include the formation of methylene blue, the molybdenum blue color formed by the reduction of benzidine, and the lead sulfide-stain method.

(1) **Determination as Methylene Blue.** In recent years the Mecklenburg and Rosenkraenzer reaction²⁵ for determining sulfur as sulfide has received considerable attention.^{18, 26-30} An acidic solution of a sulfide reacts with *p*-dimethylaminoaniline monohydrochloride in the presence of an oxidizing agent such as ferric chloride to produce methylene blue, which is then determined spectrophotometrically. The reaction is not quantitative, but reproducible results can be obtained if conditions are carefully controlled. The concentrations of the zinc acetate that is used to absorb the hydrogen sulfide, as well as the ferric chloride and the temperature at which the color is developed, influence the results considerably. The optical density of the test solution is compared with a curve obtained with known amounts of sulfide. Cadmium sulfide, diluted with potassium chloride and thoroughly mixed, may be used as a standard. The curve of sulfur concentration vs. the logarithm of the transmittancy is essentially a straight line.

Spectral transmittancy curves for pure methylene blue and for methylene blue as prepared by this method are compared in Fig. 8.5. The peak at $668\text{ m}\mu$ is utilized in this procedure. Colored ions will interfere. Uranium interferes with the quantitative formation of methylene blue, perhaps by oxidation of some sulfide to free sulfur.

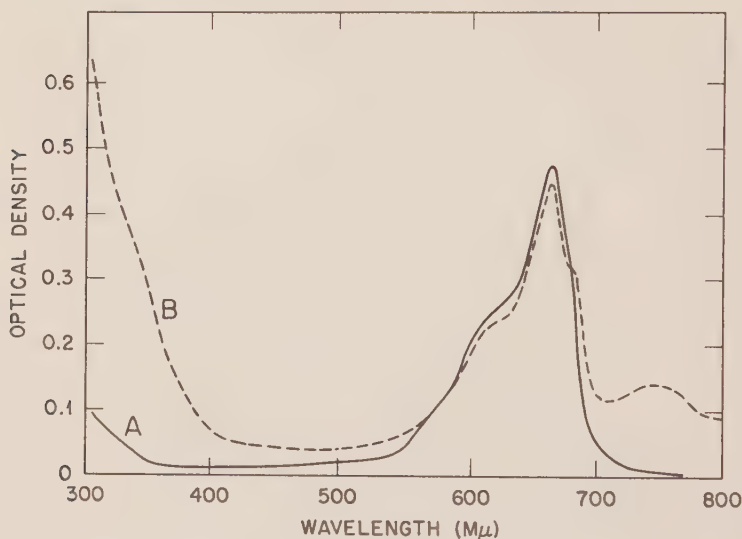


Fig. 8.5—Spectral transmittancy curves for methylene blue. A, pure methylene blue in aqueous solution; B, methylene blue formed by the reaction of sulfide with ferric chloride and *p*-dimethylaminoaniline.

The sulfide is isolated from possible interference by distillation as hydrogen sulfide. Only selenium will interfere when distillation is used. The range is 1 to 100 γ of sulfide ion.

Procedure.²⁸ An 8-ml sample of 0.6 per cent zinc acetate solution (33.9 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 31.7 g of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ are dissolved in 1,000 ml of H_2O , the solution being cleared with about 5 ml of glacial $\text{HC}_2\text{H}_3\text{O}_2$, and 9 ml of the solution is diluted to 30 ml as needed) is placed in a 10-ml measuring cylinder to absorb the distilled H_2S . The weighed sample is transferred to the distillation cell (see Fig. 8.6), the stopper containing the addition funnel is inserted, the air in the cell is displaced with purified nitrogen, and 10 ml of 1N HCl is added to the sample through the addition funnel. The generator is placed in a boiling-water bath and swept with nitrogen for 15 to 20 min. One milliliter of the *p*-dimethylaminoaniline solution (2.72 mg of *p*-dimethylaminoaniline in 5 ml of 6N HCl prepared as needed) and 0.05 ml

of the 0.1M FeCl_3 solution (13.5 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 250 ml of HCl diluted to 500 ml with H_2O) are added to the contents of the measuring cylinder and mixed well. The cylinder is immersed in a 30°C water bath for 2 hr. The solution is diluted to 10 ml, and the optical density of the solution is measured at $668 \text{ m}\mu$.

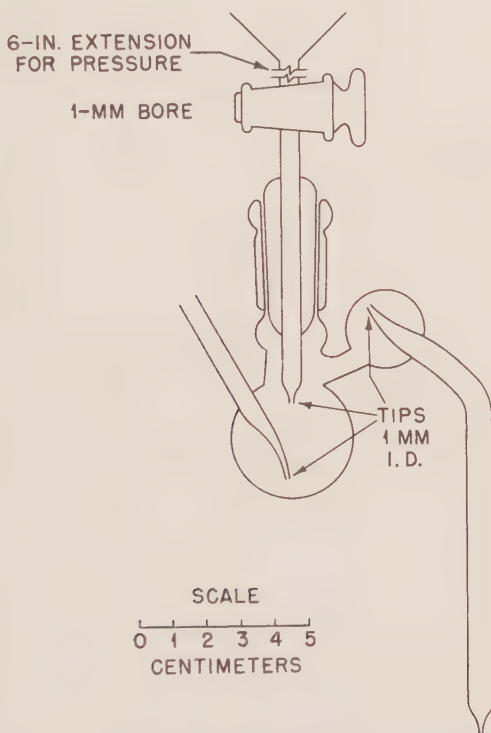


Fig. 8.6—Sulfide distillation cell.

(2) Benzidine Method. After conversion of the sulfur to benzidine sulfate, the precipitate of benzidine sulfate can be used to determine sulfur colorimetrically by spectrophotometric measurement by utilizing the blue color formed when phosphotungstomolybdic acid is reduced by benzidine.^{31, 32}

The color test for benzidine is quite sensitive, but the method is limited by the solubility of benzidine sulfate. This procedure was used for the analysis of water samples containing 0.2 to 1.0 mg of sulfate, an average loss of 0.16 mg of sulfate being reported.

Procedure.³¹ Five milliliters of the evaporated solution (representing 100 g of the unevaporated solution) is measured into a conical

glass-stoppered centrifuge tube. Three milliliters of a 10 per cent acetone solution of trichloroacetic acid and 1 ml of a freshly prepared acetone solution of 5 per cent benzidine are added to the solution. After centrifuging for 5 min the supernatant liquid is decanted, and the precipitate is washed in 5 ml of 0.2N HCl and transferred to a 500-ml graduate. One milliliter of 5 per cent gum arabic solution (treated with bromine water to destroy reducing agents, whereupon the excess bromine is boiled off) is added, followed by 1 ml of phosphotungstomolybdic acid (100 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ is dissolved in 700 ml of H_2O , and the solution is refluxed for 8 hr with 50 ml of 85 per cent H_3PO_4 and 100 ml of HCl). The solution is allowed to stand for 3 min to allow the reaction to go to completion. Three milliliters of 16 per cent Na_2CO_3 solution is added, followed 3 min later by 2 ml of 2 per cent Na_2SO_3 solution (freshly prepared). The solution is diluted to 500 ml, and the transmittancy is read at 750 m μ . A blank is carried through from the addition of the HCl.

(3) Lead Sulfide-stain Method. The distillation of hydrogen sulfide from an acid-soluble sulfide has already been discussed. Micro amounts of sulfide may be estimated by the stain produced on a strip of paper or on a length of thread impregnated with lead acetate in a manner similar to the Gutzeit test for arsenic.³³⁻³⁵

Sulfites and thiosulfates are reduced to hydrogen sulfide in the presence of a reducing agent such as aluminum. Other oxidation states of sulfur are reduced, and acid-insoluble sulfides are made soluble by fusion with an alkali or an alkaline-earth metal. Calcium has been used, because it was available with a low sulfur content. None of the common elements except selenium interferes with this test.

The procedure of Dyas, Goldsmith, and Schwob^{33,34} has a range of 0.2 to 0.7 γ of sulfur with an accuracy of about 20 per cent. A blank determination gives a value of about 0.1 γ . The apparatus used, which is a modification of the evolution flask of Scherer and Sweet,³⁵ is shown in Fig. 8.7.

Procedure.³⁴ A weighed sample and 10 to 20 mg of pure calcium are placed in a 5-ml pyrex test tube, which is heated cautiously in a microburner flame until the tube softens; either the metal or the metal vapor should come in contact with all parts of the sample. The hot test tube and its contents are then dropped into the reaction flask A, which contains 5 ml of water. (If the tube does not break, a glass rod is used to disintegrate it.) The flask is then immersed in an ice bath, and 0.5 g of Al metal and 10 ml of HCl (1 to 2) are added. The male joint contains a wad of cotton at B. An impregnated thread (cotton, white, No. 8, is impregnated three times with an aqueous solution, 5 per cent in starch and 2 per cent in lead acetate, stretched, allowed

to dry under tension, cut into 15-cm lengths, and kept in a closed container in the dark) is quickly introduced into C with 2 cm projecting from the top for ease in removal. The flask is then transferred to a thermostat at 30°C for 1 hr.

The thread is removed, the length of the stain is measured, and the sulfur content is determined by reference to a standard curve made by running samples of known sulfide content.

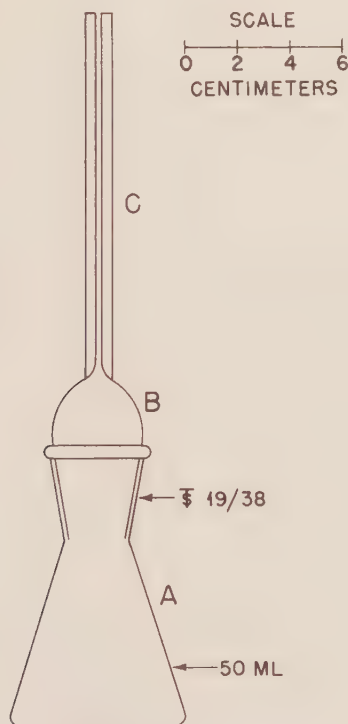


Fig. 8.7—Sulfide evolution flask.

It was found that the length of the stain is a linear function of the amount of sulfur present, and that a stain 26 mm in length is equivalent to 0.3 γ of sulfur.

(d) Turbidimetric Method. Small concentrations of sulfate are readily determined by adding barium chloride in the presence of hydrochloric acid and sodium chloride and comparing the turbidity produced with the turbidity of standard samples treated in the same

manner. A Klett colorimeter-nephelometer or Hellige turbidimeter may be used to measure the turbidity,³⁶⁻³⁹ or a spectrophotometer may be used to measure the transmittancy.³¹

Any anion whose barium salt is insoluble in 1N acid interferes. Metals forming insoluble chlorides must, of course, be removed. High concentrations of acid should be neutralized. The yellow color of uranyl ion does not interfere if the same concentration is also present in the comparison standard.

At best the method is not very accurate. In the range of 4 to 50 γ Davin et al.³⁶ reported a precision of about 15 per cent. Uranium solutions were analyzed by using a Klett nephelometer. Water containing 30 to 300 γ of sulfur was analyzed with a Coleman spectrophotometer at 350 $m\mu$.³¹ The reading on the nephelometer is almost inversely proportional to the sulfur content.

2. SELENIUM AND TELLURIUM

A turbidimetric method using a filter photometer is used for the estimation of the tellurium present. The method can be used for 2 to 10 ppm in uranium salts, with a recovery of 50 to 80 per cent.

Spectrographic methods are satisfactory for tellurium, but not for selenium. The copper-spark method will detect 0.02 γ of tellurium.

A polarographic method⁴⁰ was found to be satisfactory for the determination of tellurium in the absence of uranium and other metallic ions. The separation from interfering elements is difficult, and the method is no more sensitive than the turbidimetric method given below.

2.1 Determination of Selenium. Upon investigation of various methods for the separation of selenium from uranium and other interfering elements, distillation with hydrobromic acid was found to be the most effective. After precipitation in the elemental form the selenium in the distillate was dissolved and titrated by the method of Wernimont and Hopkinson.⁴² This titration is sensitive to 2 γ of selenium, which amounts to 0.2 ppm in a 10-g sample.⁴¹

Procedure.⁴¹ A 5-g sample of the metal is dissolved by heating gently with 10 ml of HNO_3 (1 to 1). To this is added 0.5 g of HgO . The solution is then stirred until the oxide has dissolved. A 7-ml sample of H_2SO_4 is then added, and the solution is evaporated to fumes. After fuming 15 min the solution is cooled, the sides of the beaker are rinsed down by adding a little more H_2SO_4 if necessary, and the solution is taken to fumes for another 15 min. It is then cooled and washed with 25 to 30 ml of water into a 250-ml round-bottomed flask with a ground-glass socket. A 25-ml sample of H_2SO_4 and 35 ml of $\text{HBr}-\text{Br}_2$

mixture (48 per cent HBr, containing 1 per cent by volume) are added, and the solution is distilled by using a condenser, which is fitted to the flask with a ground-glass joint and which has an extension immersed under a few milliliters of water in a small conical flask. The distillation is continued until 50 to 60 ml of distillate is obtained, which is then treated in the following manner:

A saturated solution of SO_2 is added with stirring until the Br_2 is very nearly reduced (the SO_2 solution is added drop by drop toward the end of the reaction, care being taken not to reduce the last traces of Br_2). Approximately 0.5 g of solid hydroxylamine hydrochloride is added, and the solution is warmed for 15 min on a steam bath and then allowed to stand for at least 2 hr with the beaker covered with a watch glass. (It is quite satisfactory to leave the sample overnight if necessary.) The red selenium is filtered off on a porous-bottomed porcelain micro crucible with the aid of suction and is washed thoroughly with water. The selenium is dissolved by three 1- to 2-ml portions of HBr- Br_2 mixture, and the crucible is washed six to eight times with 2-ml portions of water. (A little dark deposit is often left undissolved in the crucible. This deposit appears to be organic in nature and does not affect the results.) The filtrate is transferred (volume about 25 to 30 ml) to a 150-ml beaker. A saturated solution of SO_2 is added dropwise from a pipet until the color of bromine almost, but not quite, disappears. The sides of the beaker are rinsed down with water, and the last trace of bromine is removed with a few drops of 5 per cent phenol solution, 3 or 4 drops being added in excess. An excess of freshly prepared 0.001N solution of sodium thiosulfate is added from a buret, followed by 1 ml of 5 per cent KI solution. This mixture is stirred mechanically and titrated with 0.001N KIO_3 by using the "dead-stop" method of Foulk and Bawden.⁴³

The electrodes are suspended in the solution to be titrated (contained in a 150-ml beaker), and the solution is stirred mechanically, a voltage of 100 to 200 mv being applied by adjustment of the rheostat. Excess 0.001N sodium thiosulfate and 1 ml of 5 per cent KI are added, and the solution is titrated with 0.001N KIO_3 until a definite permanent deflection of the galvanometer is produced. Near the end point the iodate should be added in 0.1-ml portions, and the galvanometer reading should be taken after 10 to 15 sec of stirring. If the end point is passed, it is possible to back-titrate with 0.001N $\text{Na}_2\text{S}_2\text{O}_3$. It should also be possible to distinguish the end point within at least 0.1 ml of 0.001N $\text{Na}_2\text{S}_2\text{O}_3$, which is equivalent to 2 γ of selenium.

A blank is carried out on all reagents used.

2.2 Determination of Tellurium. Most of the methods described for the determination of tellurium involve its primary reduction to

the elemental form. According to the quantity present, the tellurium may then be determined gravimetrically, volumetrically, or colorimetrically. This precipitation of elemental tellurium also serves as a means of separation from a second metal, in which it usually occurs as an impurity. In the present case it was likely to be present only in

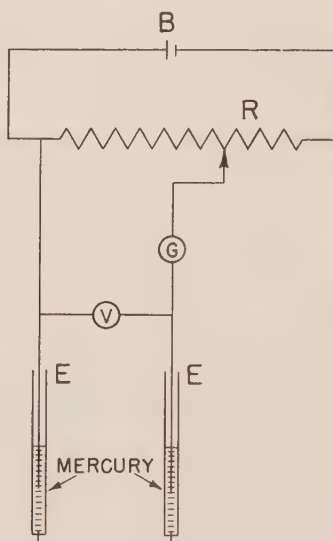


Fig. 8.8—Titration assembly. B, 2-volt accumulator, or 1.5-volt dry cell; E, platinum electrodes; G, Pye galvanometer of deadbeat-pointer type, 900 ohms resistance, 14 to 20 divisions per microampere; R, rheostat; V, voltmeter.

very low concentrations. This circumstance ruled out the final determination by gravimetric means, and the choice therefore lay between volumetric and colorimetric methods, with the additional possibility of polarographic determination.

A colorimetric method,⁴⁴ whereby the transmittancy of colloidal tellurium is measured, was found to be the most satisfactory after separating the tellurium with sodium hypophosphite.⁴⁰

Procedure.⁴⁰ A 10-g sample of drillings is weighed into a 400-ml beaker, and 25 ml of water and 20 ml of HNO_3 are added. After being covered with a watch glass, the solution is boiled gently on a hot plate until the sample is dissolved. To this solution is added 20 ml of H_3PO_4 . The solution is then evaporated until ebullition ceases, and the beaker is gradually moved toward the hottest part of the plate.

The beaker is then cooled and dissolved by warming with 100 ml of water on a steam bath. A 50-ml sample of HCl (1 to 1) and 1 ml of 0.14 per cent SeO_2 solution are added, and the solution is brought to the boiling point. The flame is removed, and 10 to 12 g of sodium hypophosphite crystals is added 2 to 3 g at a time. The mixture is stirred between each addition until the crystals have dissolved. The solution is boiled for 5 min, covered with a watch glass, and then placed on the steam bath for 1 to 2 hr.

A fairly thick pad of filter-paper pulp is prepared on a perforated porcelain disk in an ordinary funnel, pressed well down, and washed several times with an acid solution containing 25 ml of HCl and 10 ml of H_3PO_4 per 100 ml. Before the solution is filtered through this pad, it is stirred to redissolve any precipitate formed by condensed water running down the side of the beaker. After the solution is transferred, the sides and bottom are rubbed with a rubber policeman and rinsed on the filter with HCl (1 to 3). The washing of the precipitate is continued with the same acid until all the uranium and H_3PO_4 have been eliminated from the filter pad. This result is best accomplished by using a slight suction toward the end of the filtration.

The precipitate is dissolved in a mixture of Br_2 and HCl (HCl saturated with Br_2 , diluted with an equal volume of water) by pouring two 5-ml portions over the pad, collecting the solution in a 50-ml beaker, and washing well with water until the beaker is about two-thirds full. The solution is allowed to evaporate to dryness on the steam bath until no acid odors are detectable. (The selenium is removed by the evaporation.)

To this solution are added 1 ml of H_3PO_4 and 5 ml of water. The solution is then warmed to dissolve the solids. It is next cooled, and 1 ml of 1 per cent gum arabic solution and 0.05 g of sodium hypophosphite crystals are added. The solution is slowly brought to the boiling point and boiled gently for exactly 1 min, after which it is cooled and transferred to a 10-ml graduated cylinder, washing in with a sufficient quantity of water to reach the graduation mark. The absorbency is measured in a Spekker absorptiometer by using a 1-cm cell and No. 7 dark-blue filters. The amount of tellurium is read from a graph previously prepared by the reduction of known amounts of tellurium under similar conditions.

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Chapter 9

PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

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Determinations for the elements of Group V-B of the periodic table were made. The analytical chemistry of nitrogen has received special attention in Chap. 3 on "Nitrogen."

The analytical chemistry of phosphorus has been almost entirely linked with the phosphate ion. Samples of ores, intermediates, and solutions which contained the element as phosphate were analyzed. The phosphorus, if present in a different form, was converted to the phosphate before the analysis was made. Methods for the determination of phosphate ion were necessary because the relative insolubility of uranyl phosphate in feebly acid solution was an ever-present source of uranium loss. Bismuth was of analytical interest because of the insolubility of its phosphate and oxychloride in acid solution.

1. PHOSPHORUS

1.1 Methods of Solution. Uranium metal and oxides are dissolved in nitric acid. Ores and intermediates may be decomposed with various combinations of nitric, sulfuric, perchloric, hydrochloric, and hydrofluoric acids.¹⁻⁵ Fusion with sodium carbonate and sodium peroxide may also be used. Sulfuric acid is undesirable if the ammonium phosphomolybdate procedure is to be used because excess sulfate cannot be removed by fuming. At the temperature necessary for sulfuric acid fuming, phosphoric acid is lost. If metals that form insoluble phosphates in acid solution, e.g., zirconium, tin, titanium, and thorium, are present, all insoluble residues must be carefully examined. For further details on decomposition of samples reference is made to Chap. 1 on "Uranium" and to Hillebrand and Lundell.⁶

1.2 Methods of Determination. Gravimetric methods were used in which the weighing form was yellow ammonium phosphomolybdate

or its ignition product, phosphomolybdic anhydride, $P_2O_5 \cdot 24MoO_3$,^{7,8} magnesium pyrophosphate,^{4,6,9} or uranyl pyrophosphate.¹⁰

The volumetric methods were based on the alkalimetric treatment of the yellow precipitate (see references 2, 5, 6, 11), or, in the case in which total pyrophosphate was obtained, by precipitation with copper. The precipitate was redissolved in sulfuric acid, and the equivalent copper was determined by the volumetric iodide method.^{6,12}

Colorimetric methods for micro quantities based on the molybdenum blue reaction have been utilized (see references 1, 3, 7, and 13 to 17).

Spectrographic methods are discussed in Chap. 26 on "Spectrochemical Methods." Therefore they will not be treated in this chapter. Spectrographic methods are not extremely sensitive for phosphorus, the lower limit of detection being about 50 ppm.

(a) Gravimetric Methods. Weighing phosphorus as the yellow ammonium phosphomolybdate precipitate or its ignition product has not been used extensively. Details for the gravimetric determination may be found in Kolthoff and Sandell.⁸

(1) Determination as Magnesium Pyrophosphate. The precipitation of magnesium ammonium phosphate by magnesia mixture from an ammoniacal solution of the initial yellow ammonium phosphomolybdate precipitate has been the most widely used gravimetric method for phosphorus. The precipitate is ignited, and the phosphorus is weighed as magnesium pyrophosphate. Details of the method may be found in Hillebrand and Lundell.⁶ The method was adapted for use with uranium base materials.^{4,9}

(2) Determination as Uranyl Pyrophosphate. Ammonium uranyl phosphate, though soluble in mineral acids, may be precipitated quantitatively at a pH of 5.¹⁹ On ignition the precipitate is converted to uranyl pyrophosphate, $(UO_2)_2P_2O_7$, a stable weighing form. The method is most useful in the analysis of moderately pure uranium compounds or solutions, since many cations interfere by coprecipitation. The procedure is given below.

Procedure.¹⁰ A 1-g sample is transferred to a 400-ml beaker; then 10 ml of HCl and 10 ml of HNO_3 are added, and the mixture is heated on a hot plate to effect solution. The solution is evaporated to 5 ml, cooled, and diluted to 100 ml. Any insoluble matter is filtered off. The residue is then washed with 0.5 per cent HCl. The filtrate is adjusted to about 200 ml, 1 g of CH_3COONH_4 is added, and the solution is heated almost to boiling. Four drops of methyl red indicator are added, and NH_4OH is then added slowly until the solution turns a faint pink. After the solution has cooled it is filtered through a Whatman

No. 42 filter paper, and the precipitate is washed with a 1 per cent $\text{CH}_3\text{COONH}_4$ solution and is transferred to a weighed porcelain crucible, the paper is carefully smoked off, and the precipitate is finally ignited with a Meker burner. It is then cooled and weighed as $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

(b) Volumetric Methods. (1) Phosphomolybdate Method. The determination of phosphorus in the ammonium phosphomolybdate precipitate may be made by a volumetric method (see references 2, 5, 6, 11), more rapidly but less precisely than by the gravimetric method. The precipitate, when washed free of acid, may be dissolved in an excess of standard base; the excess is then titrated with standard acid. The stoichiometric relation is obeyed well enough for an accuracy of about 3 per cent in the range of 0.5 to 15 mg of phosphorus. The procedure given below is that of Krause¹¹ for analyzing uranium nitrate solutions. It is based on the method described by Hillebrand and Lundell.⁶

Procedure.¹¹ An aliquot of a slightly acid solution, containing 0.5 to 15 mg of phosphorus as phosphate, is diluted to 50 ml in a 250-ml glass-stoppered Erlenmeyer flask. The solution is heated to 40 to 50°C, and 50 ml of molybdate reagent (100 g of MoO_3 is dissolved in 400 ml of H_2O and 80 ml of NH_4OH , and the solution is filtered and slowly poured into a solution of 400 ml of HNO_3 and 600 ml of H_2O) is added. The flask is stoppered and vigorously shaken for 10 min. After an hour the solution is filtered through a Whatman No. 42 filter paper supported on a platinum filter cone by using a small amount of filter pulp and suction. The Erlenmeyer flask is carefully washed free of acid with 0.1N potassium nitrate. The washing of the precipitate is continued until 10 ml of the wash liquid fails to decolorize a drop of 0.1N sodium hydroxide plus a drop of phenolphthalein. Usually 10 to 15 washings are required. The filter paper and precipitate are transferred back to the Erlenmeyer flask. The precipitate is dissolved in 100 ml of freshly boiled water plus a measured excess of standard 0.1N sodium hydroxide solution. An excess is shown by the disappearance of the yellow color due to the phosphomolybdate complex. The excess alkali is titrated with standard acid by using phenolphthalein as indicator.

(2) Determination of Pyrophosphate. Other workers developed a method for determining pyrophosphate in a mixture containing potassium pyrophosphate, copper pyrophosphate, and orthophosphoric acid.¹² Copper pyrophosphate is determined by titrating the copper. The pyrophosphate (total) is precipitated with excess cupric sulfate, the precipitate is dissolved in sulfuric acid, and the equivalent copper is determined iodometrically.⁶

Procedure for Copper Pyrophosphate.¹² A 10-ml sample of the pyrophosphate solution is pipetted into a 500-ml Erlenmeyer flask, and about 50 ml of water is added. The solution is made acid with acetic acid, and 5 ml of glacial acetic acid is added in excess. To this mixture 10 ml of 30 per cent KI solution is added. The solution is swirled gently for a moment, is covered with a watch glass and allowed to stand for 5 min, and is titrated with standard 0.1N sodium thiosulfate solution until the brown color of the iodine has almost disappeared. A 10-ml portion of 10 per cent KSCN solution and 1 ml of saturated starch solution are added, and the solution is titrated until the purple color disappears. The swirling is kept to a minimum until the end point is almost reached.

Procedure for Total Pyrophosphate.¹² A 3-ml sample of the solution is pipetted into a 100-ml beaker, 10 drops of glacial acetic acid and 10 ml of copper sulfate solution (150 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter) are added, and the solution is allowed to stand for about 2 hr. It is then filtered through a Sela porous crucible or fritted-glass crucible (of fine porosity) and washed twice with 1 per cent acetic acid solution. The precipitate is redissolved by washing the crucible carefully with H_2SO_4 (1 to 1), and the washings are collected in a 500-ml flask. The solution is neutralized with 10 per cent NaOH and analyzed for copper by using the above method.

By accurately pipetting 10 ml of standardized copper sulfate solution for the precipitation, the filtrate and washings may be collected and analyzed for copper by the preceding method in order to determine the potassium pyrophosphate directly.

(c) Colorimetric Methods. The only colorimetric method used was the one based on the formation of molybdenum blue. An acid solution of phosphate ion will react with ammonium molybdate to form a heteropoly acid, phosphomolybdic acid, which is soluble in certain organic solvents and may be reduced with a variety of reducing agents to a blue substance of unknown composition. The intensity of the color may be measured with any of the available colorimetric or photometric instruments. A summary of the different reducing agents employed and the methods used to obtain the "blue compound" is given by Yoe.²⁰

A method using hydrazine sulfate as the reducing agent, but without extraction, was developed for the determination of P_2O_5 in ores¹ and in commercial uranium oxide.³ This method was adapted from the work of Hague and Bright.¹⁸

The use of stannous chloride as a reducing agent, both with and without solvent extraction of the blue compound, has also been exten-

sively investigated by Langham and others.^{14-17,21} When no extraction is used, a large number of ions interfere. An extraction with *n*-butyl alcohol eliminates all interferences except arsenate and germanate.²² In the presence of arsenate the results for phosphorus are high by an amount equivalent to 20 to 30 per cent of the arsenic present. Hydrobromic acid has been used to remove arsenic prior to the determination.³ Silicate, which may be determined by the same procedure except for lower acidity, does not interfere when the aqueous phase is 1N in sulfuric acid.

Considerable difficulty was experienced in removing the last traces of arsenic. Reduction with zinc, sulfur dioxide, or hydrogen sulfide, followed by evaporation with hydrochloric acid, proved inefficient. Hydriodic acid was found to be a satisfactory reducing agent. Addition of potassium iodide to the acid solution, followed by evaporation to dryness, removed arsenic completely, and a phosphorus determination was satisfactorily carried out on the resulting solution.

(1) Hydrazine Reduction Method. Procedure.³ A 0.500-g sample of commercial uranium oxide is weighed into a platinum dish. To this are added 5 ml of HNO_3 (1 to 2), 5 ml of 60 per cent perchloric acid, and 1 ml of hydrofluoric acid. The sample is heated on a steam bath for at least 90 min, with gentle swirling several times during the first 5 min to prevent spattering. It is then heated on a hot plate at medium temperature until perchloric acid fumes are evolved. The sample is cooled and diluted to 500 ml. An aliquot, usually 5 ml of the solution, is used to develop the color. With each set of determinations it is necessary to carry a blank and a standard containing 50 γ of P_2O_5 through the same procedure.

A 3-ml sample of 60 per cent perchloric acid is pipetted into each of several 125-ml Erlenmeyer flasks. One of these is for the blank, one is for the standard P_2O_5 solution, and the others are for the aliquots of the sample solutions. These solutions are added to their respective flasks, which are heated on a hot plate at high temperature until the perchloric acid refluxes almost at the neck of the flask. The flask is cooled in water, 5 ml of HBr (1 to 4) is added, and the solution is refumed. (This procedure is necessary in order to remove any arsenic that may be present.) It is cooled somewhat, and 10 ml of water and 15 ml of 10 per cent sodium sulfite solution are added. The solution is heated just to boiling, care being taken that no "bumping" occurs. A 20-ml quantity of freshly prepared ammonium molybdate-hydrazine sulfate reagent (25 ml of 2 per cent ammonium molybdate in 11N H_2SO_4 is diluted to 80 ml with water, 10 ml of 0.15 per cent hydrazine sulfate is added, and the solution is then diluted to 100 ml with water) is added, and the flasks are covered with 50-ml beakers

and digested on the steam bath for 15 min. They are then cooled rapidly by being held in a stream of cold water and are diluted to 50 ml with a mixture (1 to 4) of the ammonium molybdate-hydrazine sulfate reagent and water. The transmittancy is measured against the blank with a Fisher electrophotometer, using a No. 650 filter.

(2) Stannous Chloride Reduction Method. Procedure in the Presence of Arsenic.⁷ An aliquot portion of a nitric acid solution of the sample is evaporated just to dryness. Ten milliliters of HCl is added, and the solution is again evaporated to dryness. The hydrochloric acid treatment is repeated. The residue is dissolved in 10 ml of HCl and 10 ml of H₂O. A 5-ml sample of 10 per cent potassium iodide solution is added, and the solution is evaporated just to dryness. This treatment is repeated to remove the last traces of arsenic. The residue is dissolved in 30 ml of water and 1.5 ml of H₂SO₄ (1 to 3). Bromine water is added to the hot solution until the uranium is oxidized, as shown by the yellow color of the solution. The excess bromine is boiled off, and the solution is cooled.

After the solution has cooled, 0.5 ml of 10 per cent ammonium molybdate is added, and the solution is extracted successively with 7-, 3-, and 3-ml portions of ethyl acetate-amy alcohol mixture (1 to 2), the organic layers being combined in a small separating funnel. The combined extracts are washed with 2 to 3 ml of water, and the organic layer is run into a stoppered cylinder. Two drops of stannous chloride solution (50 g of stannous chloride in 50 ml of HCl diluted with 50 ml of H₂O) are added, and the solution is shaken well. The volume is adjusted to a known amount with the ethyl acetate-amy alcohol mixture. It is centrifuged to dry the solvent, and the transmittancy of the blue-colored solution is measured against a blank on reagents with a Spekker photometer by using No. 1 (red) filters.

For the determination of less than 2 γ of phosphate the following procedures have been used in the absence of interfering ions.

Procedure without Extraction.¹⁴ To the appropriate amount of sample solution, diluted to 0.5 ml in a 2-ml glass-stoppered test tube, are added 0.2 ml of 10N H₂SO₄ and 0.1 ml of 5 per cent ammonium molybdate solution. The tube is stoppered and mixed without wetting the stopper. After a few minutes 0.2 ml of stannous chloride solution (a stock solution of 10 g of SnCl₂ in 25 ml of HCl is diluted 300 times with H₂O) is added and mixed thoroughly. Any liquid adhering to the walls is centrifuged down. The tube is heated in a water bath for 20 min, cooled with tap water, and again centrifuged. The transmittancy is measured at 820 m μ against a blank carried through the same procedure. Results are obtained from a standard curve prepared by using known quantities of phosphate.

Procedure for Butyl Alcohol Extraction.¹⁷ The desired amount of sample, diluted to 0.45 ml, is added to a separatory funnel,¹⁶ as shown in Fig. 9.1, with 0.25 ml of 5 per cent ammonium molybdate (stored in a wax-lined container) and 0.1 ml of 10N H_2SO_4 . The solution is mixed well. After 5 min 1.0 ml of *n*-butyl alcohol is added, and the

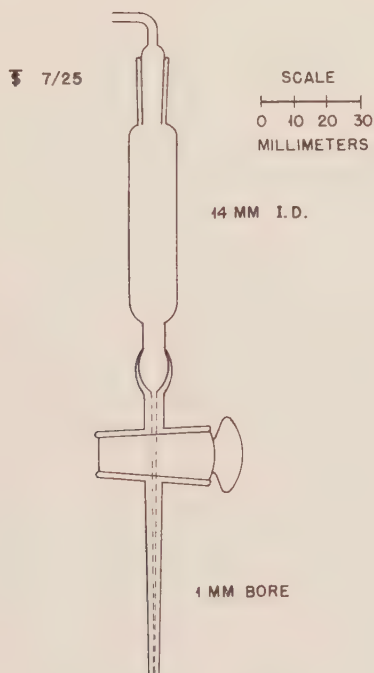


Fig. 9.1—Capillary separatory funnel.

liquids are agitated for 2 min. When the phases have separated, the water (lower) layer is discarded. The alcohol is washed for 30 sec successively with two 0.8-ml portions of 1N sulfuric acid. A volume of 1.5 ml of stannous chloride solution (as in the previous procedure) is added, and the phases are mixed for 30 sec.

The aqueous phase is discarded. The alcohol is transferred to a 1-ml volumetric flask. The funnel is rinsed with 0.2 ml of ethanol, which is added to the flask. The solution is diluted to volume with ethanol. (Enough alcohol is lost by solution in the aqueous phases to make the volume at this point less than 1 ml.) The solution is mixed and transferred to a 4-ml absorption cell. (A special cell block, as

shown in Fig. 24.3 of Chap. 24 on "Photometric Methods" makes possible the measurement of 1 ml of solution. If the highest sensitivity is not required, the solution may be diluted to a larger volume, thus eliminating the need for a special cell holder.) The transmittancy is measured against water at 730 $m\mu$ and compared with a graph obtained by using known quantities of phosphate.

2. ARSENIC

The Gutzeit method has been found satisfactory and convenient for the routine determination of various types of uranium samples.

Arsenic in the absence of phosphate and germanate may be determined by the molybdenum blue method described previously for phosphorus. The reactions of arsenate and phosphate are completely analogous.

The volumetric iodine method, subsequent to an arsenic trichloride distillation, appears to be the most desirable method for the accurate determination of macro concentrations of arsenic.

Arsenic is also determined by spectrographic methods, which are discussed in Chap. 26 on "Spectrochemical Methods."

2.1 Methods of Solution. The volatility of arsenic trichloride must be considered during the preliminary treatment of samples. An oxidizing agent such as nitric acid must be present during solution of the sample and during prolonged heating or evaporation in order to prevent the reduction and loss of arsenic. Uranium-bearing ores are fused with sodium carbonate and potassium nitrate, the melt being taken up with water and sulfuric acid.²³ Uranium metals and oxides are readily dissolved in nitric acid.

2.2 Methods of Separation. The precipitation of arsenic pentasulfide from strong hydrochloric acid solution will separate arsenic from most other ions, including uranium, germanium, copper, molybdenum, and mercury.⁶

2.3 Methods of Determination. (a) Gravimetric Method. Determination as As_2S_3 . A gravimetric method for macro quantities of arsenic, particularly in ores, has been used.²³ The method is based on the work of Scherrer.²⁴ The arsenic is separated by the distillation method; it is precipitated from hydrochloric acid solution as As_2S_3 and weighed as such. Germanium and selenium interfere and thus must be absent.

Procedure.²³ A suitably sized ground sample containing not more than 50 mg of arsenic is mixed with an equal weight of potassium nitrate and eight times its weight of anhydrous sodium carbonate, and the mixture is fused in a porcelain crucible. The melt is taken up

with water, and the solution is carefully acidified with H_2SO_4 (1 to 1). The solution is then heated to dissolve the salts. It is filtered, and the residue is washed with hot water. The filtrate is evaporated several times on a steam bath and transferred to a Scherrer distillation apparatus²⁴ by using HCl (1 to 1) as a wash solution. A 1-g sample of KBr and 3 g of hydrazine sulfate are washed into the apparatus by means of the same wash solution. The volume should be about 100 ml. A stream of CO_2 is passed through the apparatus at the rate of about six to eight bubbles per second. The solution is boiled gently until the volume in the distilling flask has been reduced to 50 ml. The temperature should be about 111 to 112°C at this stage. Without interrupting the stream of CO_2 or the heating, the receiver is removed, and the end of the condenser is rinsed with distilled water. The distillation is repeated after adding 25 ml more of HCl (1 to 1). The two distillates are then combined.

The sulfide is precipitated at room temperature by a rapid stream of hydrogen sulfide. The mixture is allowed to stand until the precipitate has settled, whereupon it is filtered through a tared sintered-glass crucible. The precipitate is washed with HCl (1 to 1) and saturated with H_2S , then with alcohol, next with carbon disulfide to remove any free sulfur, and finally with alcohol. It is then dried to constant weight at 110°C.

(b) Volumetric Method. Determination with Iodine. The distillation of arsenic trichloride yields a solution of arsenious acid free from most other reducing agents. The arsenic may be determined by direct titration with iodine in the presence of bicarbonate by using starch as the indicator.

Procedure.⁷ About 2 g of oxide or metal is dissolved in HNO_3 , and the solution is evaporated almost to dryness. A 20-ml portion of H_2SO_4 (1 to 1) is added, and the solution is evaporated to fumes of SO_3 . After cooling, a few milliliters of water are added, and the evaporation to fumes is repeated several times until all the HNO_3 has been removed. A 100-ml volume of water is added to the cold solution, which is then boiled. It is next rinsed into an all-glass distillation apparatus, and 3 g of KBr and 1 g of hydrazine sulfate dissolved in a little water are added, followed by 50 ml of HCl . A thermometer is fitted into the liquid through a ground-glass socket. The solution is distilled until the temperature starts to rise above 108°C, when the distillate is collected under water. The distillate is neutralized to litmus paper with ammonium hydroxide while being cooled under running water. The minimum excess of HCl is added, and the solution is cooled to room temperature. After neutralizing with NaHCO_3 several grams in excess are added, and the solution is titrated with 0.5N iodine to a blue

color with starch indicator. A second distillation should be carried out with the same amount of HCl and water. A blank test is carried out with the same quantities of reagents.

(c) Colorimetric Method. Gutzeit Method. For the routine determination of arsenic as a trace impurity in various uranium samples, the Gutzeit method^{6,25} has been found satisfactory and convenient. The following procedure was used on commercial uranium oxide.

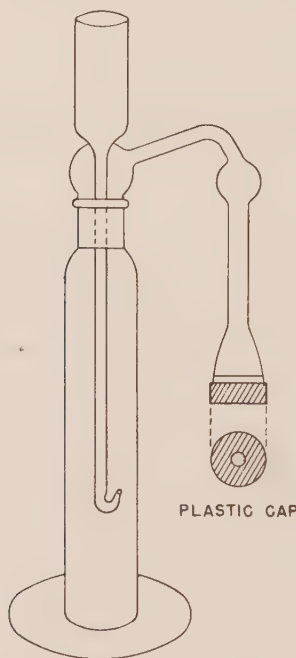


Fig. 9.2—Gutzeit apparatus.

Procedure.²⁷ A 5-g sample is dissolved by heating on a steam bath in a mixture of 15 ml of HNO_3 and 15 ml of H_2O . Five milliliters of HCl is added, and the solution is evaporated to dryness. This residue is dissolved in 30 ml of H_2O and 5 ml of HCl and is filtered. Any remaining residue is washed, and the filtrate is made up to 500 ml. The solution is mixed well and tested for arsenic as follows:

A 5-g sample of zinc (A. R. granulated 20 mesh) is placed in a Gutzeit apparatus (see Fig. 9.2), and two plugs of lead acetate cotton are inserted in the neck of the apparatus. A disk of HgCl_2 paper

(circles to fit the plastic cap are cut from Whatman No. 40 filter paper, saturated with a 5 per cent solution of HgCl_2 , and air-dried) is inserted in the cap, and the cap is screwed tightly in place.

A 1-ml sample of the solution is transferred to the Gutzeit apparatus. Three drops of bromine water and 10 ml of HCl (5 to 95) are added, followed in a few minutes by 3 drops of 10 per cent KI solution. Hydrochloric acid is then added (3 or 4 ml at a time) as needed until the zinc has dissolved. The plastic cap is finally removed, and the stain on the paper is compared with standards.

3. ANTIMONY

3.1 Methods of Solution. Because of the volatility of its chlorides, antimony may be lost if evaporations to dryness are included in the preliminary treatment of the samples. Its salts hydrolyze readily to form insoluble basic salts, and the antimony solutions should be kept rather strongly acid unless a complexing agent such as tartrate is present.

3.2 Methods of Separation. Separation as sulfide was quite satisfactory even for a few micrograms of antimony, provided that 1 or 2 mg of arsenic was added to the solution to act as a carrier.

3.3 Methods of Determination. For large concentrations the volumetric permanganate method as described by Hillebrand and Lundell⁶ and by Scott²⁸ has been useful. Spectrographic methods have been found satisfactory for the determination of trace amounts. These methods are described in Chap. 26 on "Spectrochemical Methods." A colorimetric method, the pyridine-iodide method, is described below.

Colorimetric Method. **Pyridine-Iodide Method.** Antimony may be determined by measuring the golden-yellow color produced by trivalent antimony with pyridine and potassium iodide in acid solution.^{7,13,29} Sulfurous acid is added as a reducing agent in order to prevent coloration of the solution by the oxidation of iodide to iodine. Gum arabic stabilizes the suspension of yellow pyridine antimony iodide.

Tin and arsenic do not interfere. Antimony is separated from other metals by adding arsenic as a carrier, precipitating in acid solution with hydrogen sulfide, and dissolving with ammonium sulfide as in the usual qualitative analytical procedure.

In the absence of metals with insoluble iodides and of oxidizing agents the test may be applied directly to the sample solution, with the sulfide separation omitted.

Procedure.¹³ Uranium metal and U_3O_8 are dissolved in HNO_3 (1 to 1). Uranium hexafluoride is dissolved in water, a slight excess of

H_2SO_4 is added, the solution is taken to fumes, and the residue is then dissolved in H_2O .

To an appropriate amount of sample solution (after the removal of any fluoride present) is added 5 ml of H_2SO_4 . After heating to fumes, the solution is cooled and diluted with 100 ml of water. An arsenious solution containing 2 mg of arsenic is added, and the solution is heated to boiling and saturated with hydrogen sulfide. When the precipitate has coagulated, it is filtered on a Whatman No. 40 filter paper and washed with hydrogen sulfide water. The sulfides are then dissolved with warm ammonium sulfide solution. The resulting solution is evaporated with 5 ml of H_2SO_4 to a low bulk, a few drops of HNO_3 are added, and the solution is again evaporated to fumes to remove nitric acid. When cool once more, the solution is diluted with 15 ml of water.

In another beaker are mixed, in order, 5 ml of 10 per cent gum arabic, 5 ml of 10 per cent potassium iodide, 0.5 ml of 20 per cent pyridine, 0.5 ml of one-tenth saturated sulfur dioxide solution, and 20 ml of H_2SO_4 (1 to 3). The test solution is added with continual stirring. After 2 or 3 min the transmittancy of the solution is measured against a blank by means of dark-blue filters.

4. BISMUTH

4.1 Methods of Solution. Bismuth is readily dissolved in nitric acid and presents no special problem in the treatment of metallurgical samples. Its tendency to hydrolyze and precipitate as basic salts requires that its solutions be kept fairly acid. Unlike arsenic and antimony, in the case of bismuth there is no danger of loss by volatilization of its chloride.

4.2 Methods of Separation. The reaction with dithizone cannot be used to separate bismuth completely from uranium solutions.³⁰ A chloroform extraction of the cupferrate, however, has been used for the separation of bismuth from uranium.

4.3 Methods of Determination. Bismuth may be determined by a variety of methods: gravimetrically as bismuth phosphate; volumetrically by the 8-hydroxyquinoline iodide method; colorimetrically with dithizone, tetraphenylarsonium chloride, or potassium iodide; polarographically; and spectrographically. The latter two methods are discussed in Chap. 26 on "Spectrochemical Methods." The range of the methods employed is given in Table 9.1.

(a) Gravimetric Method. Determination as Bismuth Phosphate. Macro amounts of bismuth may be precipitated and weighed as bismuth phosphate.³¹⁻³³ In 0.1N nitric acid the solubility of bismuth phosphate is approximately 0.1 mg per liter at 30°C. In the presence

of excess phosphate the solubility is negligible. However, since the solubility increases rapidly with increasing acidity, the acidity must be less than 0.5N, and preferably as low as 0.1N.

Titanium, zirconium, hafnium, thorium, tin, columbium, and tantalum must be absent. Many other metals, although soluble in the absence of bismuth, are coprecipitated with the bismuth phosphate, and these interfere if present in moderate concentrations. Chloride

Table 9.1—Range of Methods for Determination of Bismuth

Method	Range
Gravimetric:	
Bismuth phosphate	1–500 mg
Volumetric:	
Oxine-iodide	0.1–50 mg
Colorimetric:	
Dithizone	2–50 γ
Tetraphenylarsonium chloride	5–1,000 γ
Potassium iodide	10–1,000 γ
Polarographic:	1–50 mg
Spectrographic:	
Carrier distillation	Limit 0.5 ppm
Copper spark	0.05–10 γ

is undesirable because of the possible formation of bismuth oxychloride, which is also quite insoluble at the acidity used. In the absence of interfering elements, quantities of bismuth up to 500 mg may be determined with an accuracy of 0.2 per cent.

Procedure.^{31,32} To a sample of solution containing less than 0.5 g of bismuth and no interfering ions, ammonium hydroxide is added until a permanent precipitate forms. The solution is then acidified with 2 ml of HNO_3 , diluted to 250 ml, and heated to about 75°C. The bismuth is precipitated by the addition of 40 ml of 10 per cent $(\text{NH}_4)_2\text{-HPO}_4$. After digesting 1 hr on a steam bath, the solution is filtered through a sintered-glass crucible, and the precipitate is washed with 0.1N HNO_3 , dried at 120°C, and weighed as BiPO_4 .

(b) Volumetric Method. Oxine-Iodide Method. Milligram quantities of bismuth may be determined by precipitation as 8-hydroxyquinoline tetraiodobismuthate, $(\text{C}_9\text{H}_7\text{ON})\text{HBI}_4$, followed by volumetric determination of the iodine in the precipitate by titration according to the Lang method.³⁴⁻³⁷

The compound 8-hydroxyquinoline tetraiodobismuthate is insoluble in dilute acid. After it is washed to remove excess iodide, it is dissolved in more concentrated acid. Potassium cyanide is added, and the iodide is then titrated with standard iodate, using starch indicator. Free iodine is first formed, but as more iodate is added, the iodine is quantitatively oxidized to iodine cyanide. The end point is indicated by the disappearance of the blue starch complex.

Mercury, silver, lead, and thallium, forming insoluble iodides, will interfere. The same holds true for an excessive concentration of hydrochloric acid.³⁵

A 1-mg sample of bismuth can be determined with an accuracy of 1 per cent.

Procedure.³⁴ To 5 to 10 ml of a cold solution, less than 1N in H_2SO_4 or HNO_3 , are added 5 ml of oxine solution (3 per cent 8-hydroxyquinoline in 0.2N H_2SO_4) and, dropwise with shaking, 5 ml of 0.1N potassium iodide. After 15 to 30 min the precipitate is filtered on a sintered-glass disk and washed with several 5-ml portions of wash solution (15 ml of 6N H_2SO_4 , 25 ml of 0.1N potassium iodide, 1.8 g of oxine, and 0.8 g of hydrazine sulfate diluted to 1 liter). It is dried for 5 min with suction. The precipitate is then dissolved in 6 ml of 4N HCl , is transferred to a glass-stoppered flask, and, after the addition of 0.6 ml of 0.5N KCN , is diluted to 15 ml. The iodide is titrated, using starch indicator, with standard KIO_3 (2.048 g of KIO_3 per liter, which is equivalent to 1 mg of bismuth per milliliter) until the blue color disappears. The titration should be performed under a hood, and the stopper should be kept in the flask, except when the reagent is being added, in order to avoid exposure to hydrogen cyanide.

(c) Colorimetric Methods. (1) Dithizone Method. Dithizone (diphenylthiocarbazone) will react under certain conditions with many metals to form colored compounds, which may be extracted with chloroform.²⁹ In a slightly basic solution containing cyanide, only bismuth, lead, thallium(I), and tin(II) will react. The excess dithizone may be washed from the chloroform with water containing ammonium hydroxide and potassium cyanide. Interference of tin is prevented by oxidation to the stannic state. The presence of pyrophosphate will prevent thallium interference.³⁰ A clean separation of bismuth from uranium(VI) and lead may be obtained by extracting a slightly acid solution containing cupferron with chloroform; bismuth cupferrate goes into the organic phase, while lead and uranium(VI) do not.³⁰

Williams,³⁰ whose procedure as applied to uranium metal is given below, reports that 2 γ of bismuth can be detected.

The 0.06 per cent dithizone stock solution used must be carefully purified, as follows; 0.2 g of dithizone is dissolved in 100 ml of

chloroform and extracted with ammonium hydroxide (1 to 30) until the chloroform is no longer green. The combined aqueous extracts are washed once with chloroform. The solution is acidified with hydrochloric acid, kept cool, and extracted twice with chloroform. The combined chloroform solutions are diluted to 300 ml and washed once with 50 ml of water.

Procedure.³⁰ A 2-g sample of uranium metal is dissolved in 10 ml of HNO_3 and an equal volume of water. The solution is then evaporated to 10 ml and diluted to 30 ml, and 7 ml of H_2SO_4 is added to it. After cooling, NH_4OH is added until a copious precipitate forms, followed by 2 ml of HNO_3 in excess of the amount necessary to just clear the solution. After the solution is cooled and diluted to 200 ml, it is transferred to a separatory funnel. A few milliliters of 6 per cent cupferron are added, and the solution is shaken vigorously. The solution is then extracted with three 20-ml portions of chloroform, with vigorous shaking each time. The extracts are combined and filtered through a dry Whatman No. 40 filter paper into a 100-ml beaker.

The chloroform extracts are then evaporated to dryness, 3 ml of H_2SO_4 is added to the residue, and the solution is heated to fumes. About 1 ml of HNO_3 is added dropwise, and the solution is heated to fumes until all the organic matter is oxidized. The solution is cooled and diluted to 20 ml with water; a few drops of thymol blue are added, followed by 2 ml of 40 per cent ammonium citrate solution (freed from metals by making the solution alkaline to litmus with ammonium hydroxide and extracting with dithizone solution until the chloroform is green in color). After the solution is washed free of dithizone with chloroform, ammonium hydroxide is added to the solution dropwise until it becomes just blue, and then 6 drops are added in excess. To this mixture are added 10 ml of 5 per cent sodium pyrophosphate solution (freshly prepared and treated as the ammonium citrate above) and 6 drops of 10 per cent KCN solution from a dropping bottle. The cooled solution is transferred to a separating funnel and extracted with three 7-ml portions of 0.006 per cent dithizone solution, with vigorous shaking for a few minutes during each extraction. The combined extracts are shaken with 5 ml of water and then with successive portions of 40, 30, and 30 ml, respectively, of dilute NH_4OH -KCN solution (0.5 ml of ammonium hydroxide and 5 drops of 10 per cent KCN solution diluted to 100 ml with water). The orange-red bismuth dithizonate solution is transferred to a 50-ml stoppered cylinder, diluted to 30 ml with chloroform, and filtered through a Whatman No. 40 filter paper into a 1-cm cell. The color is measured by means of blue filters and compared with a curve obtained with known quantities of bismuth.

(2) Tetraphenylarsonium Chloride Method. Several studies have shown that aryl "onium" compounds can be used for the determination of bismuth.³⁸⁻⁴¹ With tetraphenylarsonium chloride, $(\text{C}_6\text{H}_5)_4\text{AsCl}$, in the presence of iodide, bismuth reacts to form a characteristic orange-colored precipitate of tetraphenylarsonium tetraiodobismuthate, $(\text{C}_6\text{H}_5)_4\text{AsBiI}_4$, which is soluble in chloroform. A colorimetric method based on this reaction was developed as a rapid method for bismuth.⁴¹

Sulfate, chloride, nitrate, thiocyanate, oxalate, and bromide do not interfere, but phosphate, chromate, cyanide, and thiosulfate do. Phosphate may be eliminated by the addition of excess hydrochloric or sulfuric acid. One milliliter of hydrochloric acid is sufficient for 5×10^{-4} mole of phosphate ion.

Oxidizing substances interfere in the test by liberating iodine. Sulfite ion is satisfactory for eliminating this interference. Although high concentrations of sulfite interfere, 2 ml of 1 per cent sodium sulfite may be tolerated. This amount is sufficient for concentrations of oxidizing substances normally encountered. If the quantity of oxidizing substances in the sample is known to be high, an aliquot of the sample should be titrated with sulfite by using starch and iodide as indicators to determine the required amount of sulfite.

Antimony, cadmium, copper, lead, mercury, and silver form interfering precipitates. Gold, platinum, and tellurium give interfering colors. Aluminum, arsenic, barium, chromium(III), cobalt, magnesium, manganese(II), nickel(II), potassium, and sodium ions do not interfere.

With the procedure given below, amounts of bismuth from 5 γ to 1 mg may be determined with an accuracy of 5 per cent. The method has also been used successfully for the analysis of uranium nitrate solutions with a lower limit of 2 γ ,⁴¹ by using only 3 ml of chloroform and special cuvettes.

Procedure.⁴¹ To an aliquot of the sample (45 ml or less) in a 150-ml stoppered separatory funnel are added 1 ml of HCl and 2 ml of 0.08M Na_2SO_3 . The solution is diluted to about 50 ml, and to it are added 10 ml of potassium iodide solution (100 g of KI dissolved in a liter of water) and 10 ml of tetraphenylarsonium chloride solution (1.14 g of reagent dissolved in water, diluted to 250 ml, and kept in a glass-stoppered bottle in a cool, dark place; the solution should be freshly prepared every week). After 15 sec of shaking, exactly 10 ml of chloroform is added. Any precipitate that adheres to the neck or stopper of the funnel is carefully washed down with a stream of distilled water. After 30 sec of shaking, the phases are separated, and

the chloroform layer is withdrawn into a cuvette (filtering the solution if it is necessary to remove any turbidity or water globules). The transmittancy is measured at $510\text{ m}\mu$ against a blank prepared in exactly the same manner as the sample.

(3) Potassium Iodide Method. In the presence of an excess of iodide ion, bismuth forms an amber or yellow solution containing the tetra-iodobismuthate ion, BiI_4^- .^{29,42-45} Platinum, palladium, antimony, and tin form colored compounds, whereas lead, thallium, mercury, and silver form insoluble iodides. Oxidizing agents that liberate free iodine also interfere, and these must be removed. The small amount of sulfite ion that is added in the test will eliminate some oxidizing substances. Large concentrations of uranium do not interfere.⁴²

The colored product formed is soluble in the higher alcohols and esters, and an extraction with amyl alcohol and ethyl acetate mixture has been used to separate it from a solution containing other colored ions.²⁹

Procedure.⁴² To 40 ml, or less, of the sample solution are added 2 ml of HNO_3 , 1 ml of saturated sulfur dioxide water, 5 ml of 30 per cent KI, and enough water to make the volume 50 ml. The transmittancy is measured at $460\text{ m}\mu$ with a spectrophotometer or compared in Nessler tubes with a blank, to which a standard bismuth solution is added from a buret until the colors match.

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Chapter 10

SODIUM, POTASSIUM, RUBIDIUM, AND CESIUM

By L. G. Bassett and W. Byerley

Because of the relatively large neutron-absorption cross section of lithium it was necessary to examine many and varied materials for this element. Satisfactory spectrographic methods developed for this element and other members of the alkali metals are treated in Chap. 26 on "Spectrochemical Methods." A recent review¹ considers the methods used for the analysis of the alkali metals through the year 1940.

1. METHODS OF SEPARATION

Before considering the individual methods of determination of the alkali metals, it should be mentioned that it has often been necessary to separate the group from large quantities of uranium. This has been accomplished by various methods such as precipitation of the uranium with 8-hydroxyquinoline,² use of peroxide,³ double precipitation with ammonium hydroxide,⁴ the use of 1-nitroso-2-naphthol followed by amyl alcohol extraction and ammonium hydroxide precipitation,⁵ precipitation of the uranium with hydrogen peroxide followed by tannic acid-aniline extraction,⁶ electrolytic reduction in the presence of fluoride ion, and extraction of the uranium(IV) as the chloroform-soluble cupferrate. The last three separation methods have been used preceding spectrographic determination.

1.1 Chloroform-Cupferrate Separation. With the chloroform-cupferrate method, any substance that prevents the extraction of the major constituent or oxidizes the reagent must be removed prior to extraction. If the sample is to be prepared for spectrographic analysis by the copper-spark method, sulfates interfere because sulfuric acid cannot be evaporated on the surface of a copper electrode.

The extraction apparatus used is shown in Fig. 10.1. A syringe and pipet are mounted on a brass frame, which is adjustable vertically and can be rotated about vertical and horizontal axes. The pipet is centered over the quartz cups, which are held in a brass rack on a

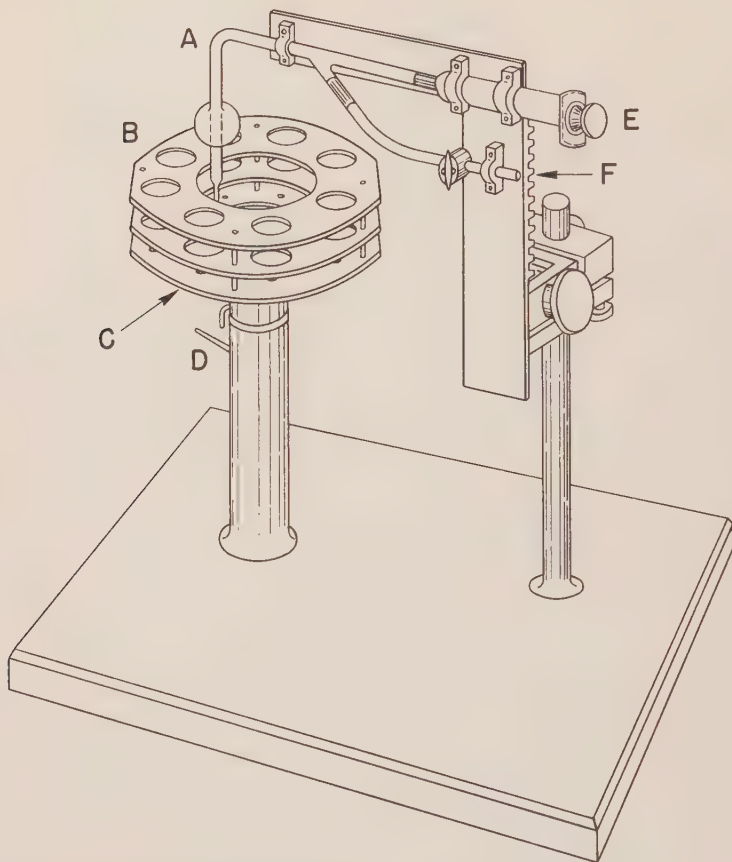


Fig. 10.1—Cupferron extraction apparatus. A, quartz pipet; B, cup rack; C, table; D, handle for adjustment of table; E, syringe; F, nitrogen inlet.

revolving table. The table also moves up and down on a spring, permitting the separation of the chloroform layer from one cup and its discharge into an adjacent cup by moving the table around the fixed pipet. The apparatus was found effective in lowering contamination of the sample due to handling, contact with ground-glass or ground-quartz surfaces, and contact with greased stopcocks.

The quartz cups in which the extraction is conducted are 35 mm high and 15 mm in diameter. A constriction is pressed into the cup 10 mm from the top. The constricted collar is 10 mm in diameter. The bottom of the cup should be an almost perfect hemisphere of 7.5 mm radius.

The critical specification in the fabrication of a 0.1-ml quartz pipet is the delivery tip, which must be no more than 1 mm in outside diameter, thin-walled, and cut or ground square. Unless these conditions are met, the liquid delivered tends to adhere to the outer wall of the pipet, and an accurate measurement is impossible.

Procedure. A sample of 1 to 2 mg is dissolved in 1N HNO_3 (distilled from quartz) or HCl (H_2O in quartz flask saturated with purified HCl) in a quartz cup and is made up to 0.5 ml in 1N acid. One milliliter of cupferron solution (Eastman, 6 per cent aqueous solution in quartz) is added, and the mixture is agitated with nitrogen for 2 min; after this 0.5 ml of CHCl_3 (redistilled from pyrex and stored in pyrex) is added and agitated for another 2 min. The CHCl_3 is withdrawn. The addition of the cupferron and the extraction with CHCl_3 are repeated, and the solution is then washed with another addition of 0.5 ml of CHCl_3 . The quartz cup is removed from the extraction apparatus, and the solution is evaporated to dryness under an infrared lamp, care being taken not to heat so strongly as to cause bumping or spattering of dry salts. The cup is removed and cooled; if the sample was made up in HNO_3 , 0.1 ml of HCl is added, and the solution is evaporated to dryness again. It may be necessary to repeat this operation if all the ammonium salts and residual organic matter are not destroyed by the first treatment. The sample may now be taken up in 0.1 ml of 1 per cent HCl for the final determination. For the spectrographic analysis the solution is coated on a pair of copper electrodes.

Quartz containers are always used for aqueous and acid solutions. They are soaked in HNO_3 , washed with a stiff brush and Duponol soap, rinsed copiously with hot distilled water, and then rinsed with cold redistilled water. All operations are conducted under a glass cover. The extractions are made in a glass case. The extraction and preparation rooms are supplied with filtered air at a positive pressure with respect to the surrounding room. The analyst wears rubber gloves during all operations. The nitrogen that is used for agitation of samples during extraction is purified by bubbling through H_2SO_4 , pyrogallol, and redistilled water.

1.2 Electrolytic Separation. The separation of excess uranium by electrolytic reduction in the presence of hydrofluoric acid, followed by a cupferron extraction, has been used before the colorimetric de-

termination of sodium and the spectrographic analysis of other alkali metals. Recoveries range from 50 to 100 per cent.

Procedure. Ten grams of metal is weighed into a large platinum dish and dissolved in HNO_3 (1 to 1). To this is added 10 ml of H_2SO_4 , and the solution is evaporated carefully to fumes of SO_3 . The excess acid is boiled off until the mass is just dry. The dish is cooled, and the residue is dissolved in water; after this 15 ml of prepared HF (anhydrous HF passed into water using polythene tubing and an inverted polythene funnel) is added and diluted to fill the dish. The solution is electrolyzed at a current of 3 amp, 10 to 15 volts, for 5 or 6 hr, or overnight. The anode consists of a platinum spiral dipping into the liquid, and the dish itself is made the cathode by resting it upon a copper-wire ring connected to the negative pole. At the end of the above period the dish is removed, and the contents are filtered, using polythene funnels and beakers, through a Whatman No. 40 11-cm filter paper previously well-washed with water. The precipitate is washed with water and discarded. (The deposit of UF_4 is cleaned from the dish by treatment with dilute NH_4OH and H_2O_2 .) The filtrate is returned to the clean dish and again electrolyzed for 5 to 6 hr under the same conditions as before. The filtrate is returned to the clean dish, which should show no yellow color due to uranium, and is evaporated to dryness in order to remove the excess sulfuric acid.

The residue is dissolved in water plus a few drops of HCl and is used for the determination desired.

2. SODIUM

2.1 Methods of Determination. (a) Gravimetric Methods. Gravimetric methods for sodium have been based on precipitation with magnesium uranyl acetate as described by Caley and Foulk¹⁰ or with zinc uranyl acetate as described by Barber and Kolthoff.¹¹

(1) Magnesium Uranyl Acetate Method. The sodium is precipitated as $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$, sodium magnesium uranyl acetate, washed with 95 per cent ethyl alcohol saturated with sodium magnesium uranyl acetate, dried, and weighed.

Potassium does not seriously interfere if less than 0.10 g is present (0.25 g if 100 ml of reagent is used). Separation from lithium can be achieved if it is present in quantities of less than 1 mg.¹⁰ Calcium, magnesium, strontium, barium, and iron do not interfere.¹⁰ No interference is found with beryllium, cerium, lanthanum, neodymium, thallium, thorium, vanadium, or zirconium.¹² Columbium and tantalum interfere because they form gelatinous precipitates upon addition of the acid reagent.¹² Silica, if present, can be removed by hydrofluoric and sulfuric acids.¹²

Anions such as phosphates, oxalates, tartrates, and silicates, which precipitate uranium in acetic acid solution, must be absent. Sulfate does not interfere when barium and strontium are absent and when calcium and ammonium are low. If barium, calcium, or strontium are present in the sodium test solution, the sulfate that is usually present in the precipitating reagent should be removed.¹¹ The method has been tested in the range of 0.20 to 50 mg of sodium.^{10,13}

(2) Zinc Uranyl Acetate Method. Zinc uranyl acetate as a precipitating reagent for sodium is said to be more precise than the magnesium in the range of 8 mg or less. The sodium is precipitated in a similar manner to the preceding method but as a sodium zinc uranyl acetate.

The precipitate may be quantitatively determined several ways.¹⁴⁻¹⁶ One method is to dry and weigh the precipitate. Another method is to estimate the volume of the precipitate in a calibrated centrifuge cone and then read the amount of sodium from a standard curve prepared by measuring the volume of precipitates obtained from known amounts of sodium.

Procedure.¹⁷ A 10-g sample of uranium is weighed on a torsion balance and then transferred to a 250-ml beaker. Fifteen milliliters of HCl and 25 ml of HNO₃ are added, the mixture is heated on a hot plate until the sample dissolves, and the solution is evaporated to 10 ml. It is then diluted to about 50 ml and filtered into a 100-ml glass-stoppered graduate. It is made up to 100 ml and mixed well, and a 1-ml aliquot is pipetted into a 50-ml beaker; 25 ml of clear zinc uranyl acetate reagent is then added with stirring. (The reagent is filtered before use.) The resultant precipitate is allowed to stand for 3 to 5 min.

A fine sintered-glass crucible is washed first with 25 ml of alcohol and then with 50 ml of anhydrous ether A. R. grade. The other washings are removed from the suction flask, and the crucible is replaced for 3 to 5 min to draw air through it; it is weighed immediately. The precipitate is filtered through the crucible and washed with six 4-ml portions of the clear zinc uranyl acetate reagent. Next the beaker is washed with five small portions of a saturated alcohol solution of the triple salt, (UO₂)₃NaZn(C₂H₃O₂)₉·6H₂O. Each wash is poured into the crucible, but air is not allowed to be sucked through the filter. The walls of the crucible are carefully rinsed down using an alcohol solution of triple salt. Forty milliliters of anhydrous ether A. R. grade is poured into the beaker, and when the crucible has been sucked dry it is rinsed with 5-ml portions of the ether, the crucible being allowed to go dry before the next portion is added. The ether washings are removed from the filter flask, the crucible is replaced, and air is

drawn through the crucible for 3 to 5 min or until the precipitate is dry. The crucible is then weighed.

(b) Colorimetric Methods. In one method^{18,19} sodium zinc uranyl acetate is dissolved in hot water, and sulfosalicylic acid is used to develop the color caused by the uranium content of the salt.^{20,21}

Silicon, mercury, silver, antimony, and large amounts of phosphate interfere. However, the normal dehydration and filtration procedure is adequate for removing silicon, and phosphate can be eliminated by dissolving the precipitate from the filter paper, thereby leaving the insoluble phosphate behind.¹⁸

Potassium does not appreciably interfere if the K/Na ratio is less than 5. Barium, calcium, and magnesium do not interfere.

Large amounts of organic acids such as oxalates and tartrates must be absent.¹¹ Large amounts of uranium give high results.

The method is applicable in the range of 10 to 360 γ . When working with quantities of sodium less than 20 γ , the solution must be evaporated to dryness just before addition of the reagent. Recovery of 80 to 90 per cent of added sodium was obtained.

The following procedure for the determination of sodium in uranium can be applied to any solution by adding zinc uranyl acetate directly to a concentrated solution of the chlorides from which interfering elements have been eliminated.

Procedure.¹⁹ A 10-g sample of uranium metal is dissolved, and the uranium is separated by electrolytic reduction and precipitation of fluoride as described under the electrolytic separation. The UF_4 is filtered off on a Whatman No. 40 filter paper, using polythene funnels and beakers, and the precipitate is washed with water. The filtrate is evaporated, and the excess H_2SO_4 is removed.

The residue is dissolved in water and a small amount of HCl. Suitable aliquots of this solution ($\frac{1}{5}$ is usually convenient for normal samples) are taken, and they are evaporated to dryness on a steam bath in a 30-ml beaker. The residue is dissolved in the minimum amount of water, which is added drop by drop from a pipet, 10 ml of zinc uranyl acetate reagent is added, and the solution is allowed to stand overnight. It is then filtered on a G-4 micro glass filter, and the precipitate is washed with ethyl alcohol previously saturated with sodium zinc uranyl acetate. The precipitate is dissolved and is washed with a few milliliters of hot water through the filter into the beaker in which the precipitation was made. It is then transferred to a 50-ml stoppered cylinder, 2 ml of 5 per cent sulfosalicylic acid and 2 ml of 10 per cent sodium acetate are added, and the solution is made up to a volume of 50 ml and allowed to stand for 5 min. The yellow color is measured in a 4-cm cell on a Spekker absorptiometer with No. 7

dark-blue filters. The sodium content is read from a standard curve prepared by developing the color in known amounts of a sodium zinc uranyl acetate solution as described above. A blank is run on all reagents through the entire procedure.

3. POTASSIUM

3.1 Methods of Determination. Of the three methods most generally used for the precipitation of potassium, i.e., precipitation as the perchlorate, the cobaltinitrite, or the chloroplatinate,⁷⁻⁹ the cobaltinitrite or chloroplatinate can be used for an indirect colorimetric method of determination. It has been said that the cobaltinitrite is the more variable in composition of the two, and hence it is less suitable for an indirect method. The report by Short⁴ gives the procedure for the determination of potassium in uranium down to 5 ppm by a chloroplatinate-potassium iodide method.

The objection to the use of cobaltinitrite because of the variability in composition of the precipitate has been overcome by using silver cobaltinitrite instead of sodium cobaltinitrite. Langham^{22,23} has used the silver cobaltinitrite method for the determination of 0.1 to 2.0 γ of potassium with an average deviation of about $\pm 0.04 \gamma$ in determining 0.7 γ of potassium.

(a) **Colorimetric Methods.** (1) **Silver Cobaltinitrite.** Silver cobaltinitrite has been used for the determination of potassium by Breh and Gaebler²⁴ and by Robinson and Putnam.²⁵ The procedure given is an adaptation by Langham^{22,23} for the determination of as little as 0.3 γ of potassium.

Potassium is precipitated as potassium disilver cobaltinitrite²⁶ on standing 3 hr at 0 to 2°C. The precipitate is dissolved in sodium hydroxide, the nitrite is diazotized and coupled with α -naphthylamine sulfanilic acid reagent, and the resulting color is compared in a Klett visual colorimeter with that obtained with a standard.

The following ions interfere: ammonium, chloride (in excess of 1 γ), lead, thallium(I), mercury, barium (in excess of 0.05M), and sodium (in excess of 0.1M).²⁶ No interference is caused by 1 γ of lithium, magnesium, or aluminum sulfate.²²

Before precipitation of potassium, chloride may be eliminated by evaporating the solution to dryness in a centrifuge tube, adding 0.1 ml of HNO₃, again evaporating to dryness, and baking gently. After this process the silver cobaltinitrite reagent is added directly to the residue.

Reagents. Silver cobaltinitrite reagent: 25 g of sodium cobaltinitrite is dissolved in 150 ml of sodium nitrite solution containing 50 g of sodium nitrite. Five milliliters of silver nitrate solution contain-

ing 2.0 g of silver nitrate is added with stirring. The solution is diluted to 200 ml, 2 ml of glacial acetic acid is added, and air is passed through the solution for 5 min. After standing for 12 hr at 4 to 6°C, the reagent is filtered through a Whatman No. 42 filter paper. The reagent must be prepared fresh every two weeks, stored at 4 to 6°C, and centrifuged just before use.

Alcohol and acetone: There should be no perceptible precipitate 3 hr after treating with silver nitrate at room temperature.

Sulfanilic acid solution: 8 g of pure sulfanilic acid is dissolved in 1 liter of 5N acetic acid, specific gravity of 1.041.

α -Naphthylamine acetate solution: 5 g of solid α -naphthylamine is dissolved in 1 liter of 5N acetic acid and filtered through absorbent cotton.

α -Naphthylamine-sulfanilic acid solution: One milliliter of α -naphthylamine is mixed with 2 ml of sulfanilic acid solution. The mixture is stable for at least two weeks.

Standard potassium sulfate solution: A solution containing 1 mg of potassium per milliliter is prepared and diluted to lower concentrations as needed.

Procedure.²³ One milliliter of the solution to be analyzed is placed in a 2-ml centrifuge cone, and 0.1 ml of silver cobaltinitrite solution is added. (By using an air-driven microcentrifuge and 0.2-ml centrifuge cones the volume of sample solution can be reduced to 0.5 ml or less.) The tubes are stoppered tightly, cooled for 2 hr at 0 to 2°C, and centrifuged for 15 min to bring down the precipitate of potassium silver cobaltinitrite. (A solid-head centrifuge is used.) The samples are placed in alternate cups, and the other cups are filled with powdered dry ice in order to prevent partial solution of the precipitate during the centrifuging process. The supernatant solution is drawn off to within about 1 mm of the precipitate, using a micro suction device controlled by the mouth. Care must be taken to avoid stirring up the precipitate and to avoid drawing off any of the finely divided precipitate held at the surface of the liquid. The precipitate and the walls of the tube are washed with 0.2 ml of ice-cold water. The tube is inclined and rotated in a manner to avoid, as much as possible, the breaking up of the precipitate. The sample is centrifuged again, and the wash liquid is drawn off as before. The washing is repeated using 60 per cent acetone once and absolute acetone four times. The precipitate is dissolved in 0.5 ml of 0.1N sodium hydroxide by heating in a water bath for 10 min, the solution is transferred to a 10-ml volumetric flask, 2 ml of α -naphthylamine-sulfanilic acid reagent is added, and the volume is made up to exactly 10 ml. The color is allowed to develop for 20 min and is compared with a 0.5- γ standard, using a Klett visual colorimeter.

(2) Chloroplatinate - Potassium Iodide Method. Cuvelier²⁷ has used sodium iodide with chloroplatinate precipitation to determine 0.005 to 0.05 mg of potassium, and a report by Short⁴ describes the use of potassium iodide after precipitation of the chloroplatinate for determinations in the range of 5 to 1,000 γ of potassium in uranium. In this method potassium is isolated as the chloroplatinate, and then potassium iodide is added to an acid solution of the precipitate. The liberated iodine is measured colorimetrically.

In the procedure given by Short⁴ 100 to 1,000 γ of potassium was added to 1- and 10-g samples of uranium. It was found that 55 per cent of the potassium was recovered. The factor of 50 to 55 per cent was reasonably constant. No data were given on the precision or accuracy of the method if applied to known amounts of potassium without the uranium interference. However, the accuracy can hardly be better than a factor of 2.

Uranium can be separated by a double precipitation with ammonium hydroxide. If uranium is present to the extent of 10 g, a portion is removed by an ether extraction.

Procedure.⁴ A 10-g sample of uranium metal is weighed into a large platinum dish and is dissolved in HNO_3 (1 to 1). The solution is evaporated to a low bulk and cooled; it should be stirred constantly until a crystalline powder is obtained. This is dissolved in 60 ml of ether and transferred to a separating funnel, and the dish is washed with another 30 ml of ether. Just sufficient water is added to give a minimum water layer after shaking thoroughly, and this aqueous layer is run into the original platinum dish. Two similar extractions with small amounts of water are made, and the aqueous extracts are reextracted with ether. The ether layer is rejected.

The solution is transferred from the dish to an 800-ml beaker, and a few drops of HNO_3 are added if necessary to complete solution. The volume is made up to 500 ml, and the solution is heated to boiling. Drop by drop with stirring, NH_4OH (1 to 19) is added to the boiling solution until the liquid is distinctly alkaline; then the precipitate is allowed to settle on a hot plate at low heat. The solution is filtered through a Whatman No. 42 11-cm filter paper and washed twice with hot 2 per cent ammonium nitrate solution. The precipitate is returned to the beaker and dissolved in a minimum amount of HNO_3 , and the precipitation is repeated under the above conditions. The two filtrates are combined and evaporated to 100 ml.

Hydrogen sulfide is passed into the hot solution, and any precipitate is filtered off through a small Whatman No. 40 filter paper and washed with a small amount of H_2S water. The filtrate is evaporated to dryness in a platinum dish, and the residue is ignited gently to remove ammonium salts and then dissolved in water; if necessary a drop of

HNO_3 is added to complete solution. The solution is evaporated and transferred to a micro beaker. The evaporation is continued just to dryness. One milliliter of 5 per cent platinum chloride solution is added, and it is again evaporated just to dryness on a steam bath. The residue is treated with 1 ml of 95 per cent alcohol wash solution containing a few milligrams of K_2PtCl_6 (filtered before using), allowed to stand for 10 min, and then filtered through a micro G-4 glass filter, the precipitate being washed several times with the same alcohol. The precipitate is dissolved with hot water, the solution being allowed to run into the beaker in which the precipitation was made. The solution, of which the volume should be 10 to 15 ml at this point, is transferred to a measuring cylinder. Fifteen milliliters of 20 per cent potassium iodide and 5 ml of 1N HCl are added, and the solution is allowed to stand for 30 min. After this it is diluted to 50 ml, and the red color developed is measured on a Spekker absorptiometer using a 1-cm cell and No. 6 blue filters. The potassium blank on the above series of operations is usually 30 to 40 γ .

4. RUBIDIUM AND CESIUM

Potassium, rubidium, and cesium are similar in their properties to the extent that most methods for the determination of potassium⁹ can also be used for the determination of rubidium and cesium.

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Chapter 11

BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND RADIUM

By L. W. Neidrach, A. M. Mitchell, and C. J. Rodden

Beryllium and its salts were analyzed for their beryllium content. The determination of magnesium and calcium was made chiefly for traces in uranium and its compounds. The determination of barium and strontium was of minor importance. Samples of uranium and radium concentrates and ores were analyzed for their radium content.

The sensitivity of their spectral lines makes spectrographic analysis a very useful method for the determination of traces of beryllium, magnesium, calcium, strontium, and barium.

1. BERYLLIUM

Beryllium and its salts were analyzed by conventional methods involving the separation of interfering elements, followed by precipitation with ammonium hydroxide.^{1,2} Traces of beryllium in uranium were determined chiefly by spectrographic methods, which are described in Chap. 26. Beryllium was determined by the greenish-yellow fluorescence produced with morin in sodium hydroxide solution.^{3,4} Beryllium was also determined colorimetrically with *p*-nitrobenzene-azo-orcinol.

1.1 Methods of Solution. Beryllium metal is vigorously attacked by dilute hydrochloric or sulfuric acid. It is not soluble in nitric acid unless a drop of sulfuric acid is added. In most cases some insoluble residue remains which may be dissolved after fusing with potassium pyrosulfate.

The solubility of beryllium oxide depends on its previous treatment. When calcined at a low heat, it may be dissolved in 6N hydrochloric or in 18N sulfuric acid. If the oxide has been heated to a high temperature or fused, hydrofluoric acid proves more effective for solution.

Uranium salts are readily dissolved in nitric acid, or sulfuric and nitric acids combined, prior to the determination of beryllium.

1.2 Methods of Separation. In the analysis of beryllium metal and oxides the separation of other impurities from beryllium is the main consideration. Silica is removed by dehydration in the usual manner. Iron and aluminum can be separated by extraction of the oxinates at a pH of 4.3 to 4.6 with chloroform.⁵ The oxinates may also be removed by filtration. The beryllium may then be precipitated after decomposition of the oxinates, with ammonium hydroxide used to separate it from magnesium and the alkali metals. If much magnesium is present, a double precipitation is necessary. Uranium is separated from beryllium by extracting its 1-nitroso-2-naphtholate with amyl alcohol.^{4,6} Beryllium may also be separated from impurities by volatilization as BeCl_2 .

1.3 Methods of Determination. Beryllium is determined in beryllium metal and its salts by precipitating with ammonium hydroxide and igniting to oxide after the separation of interfering elements.

Two methods, based on those used in the analysis of aluminum, have been employed for the determination of free beryllium in beryllium metal. In one method the volume of hydrogen evolved after treating with hydrochloric acid or sodium hydroxide is collected and measured.² The other method, used by the National Bureau of Standards, is analogous to the method used for aluminum analysis.² It is based on the volatilization of beryllium chloride in a current of dry hydrogen chloride. Beryllium oxide is not volatilized or acted upon by dry hydrogen chloride under these conditions.

Other methods have been suggested for the volumetric estimation of beryllium,¹¹ depending on the titration of the hydroxyl ion that is liberated from beryllium hydroxide when it is complexed with fluoride.

(a) Determination of Total Beryllium. The method usually employed for the determination of total beryllium is precipitation of the hydroxide after separation of impurities and ignition to the oxide. Volumetric methods have been suggested.⁷ The following procedure has been employed for beryllium metal and beryllium oxide.

Procedure.⁴³ A 5-g sample is transferred to a 500-ml Erlenmeyer flask, 120 ml of H_2SO_4 (1 to 1) is added slowly until the metal is dissolved, and the solution is heated to fumes of SO_3 for 30 min. After cooling, 300 ml of H_2O and 20 ml of H_2SO_4 (1 to 1) are added, and the solution is heated until the salts have dissolved. The solution is then filtered through a Whatman No. 42 filter paper into a dry, weighed, 500-ml volumetric flask, and the paper is washed four times with hot H_2SO_4 (1 to 19) and three times with hot water.

The insoluble material is ignited in a platinum crucible at 1100°C and weighed. The SiO_2 in the residue is volatilized with 5 drops of H_2SO_4 and a few milliliters of HF . The residue is ignited at 1100°C and weighed, and the silicon content of the sample is computed.

Any residue is dissolved in H_2SO_4 (1 to 1) to ensure that all the beryllium is brought into solution. The solution of the residue from the volatilization is added to the original filtrate in the 500-ml volumetric flask and, after cooling, is diluted to the mark. The flask and contents are then weighed.

A 10-ml aliquot of the solution (containing about 0.1 g of the beryllium metal) is pipetted into a weighed glass-stoppered bottle, and the bottle and its contents are weighed. The aliquot is then transferred to a 150-ml beaker containing 50 ml of 2N $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, and the solution is adjusted to a pH of 4.5 by the addition of either H_2SO_4 or NH_4OH . Then 5 ml of 8-hydroxyquinoline (5 per cent solution in 2N $\text{HC}_2\text{H}_3\text{O}_2$) is added, and the solution is allowed to stand for 18 hr, after which it is filtered through an S & S 589 filter paper into a 400-ml beaker. The precipitate is washed with cold water.

To the filtrate are added 10 ml of HNO_3 (1 to 1) and 10 ml of H_2SO_4 (1 to 1), and the solution is evaporated to dryness on the steam bath. A 150-ml volume of H_2O is added, and the solution is boiled until the salts have been dissolved. A slight excess of NH_4OH is added, the solution is filtered through an S & S 589 filter paper, and the precipitate is washed four times with a 2 per cent NH_4NO_3 solution (slightly ammoniacal). The precipitate is ignited to constant weight at 1100°C in a 25-ml platinum crucible. The crucible is kept over concentrated H_2SO_4 while it is cooling, and the weighing is done quickly in the covered crucible.

The BeO precipitate must be corrected for the SiO_2 present therein. The BeO is treated with 2 ml of cold water and 2 ml of H_2SO_4 , and the dissolved BeO is transferred to a 250-ml beaker containing 100 ml of water and 10 ml of H_2SO_4 (1 to 1). The solution is heated to heavy fumes of SO_3 , cooled, diluted with 100 ml of H_2O , and heated until any salts present have dissolved. The SiO_2 is filtered off on a Whatman No. 42 filter paper, washed with hot water, and ignited at 1100°C in a platinum crucible. The SiO_2 is volatilized with H_2SO_4 and HF , and the residue is reignited. The weight of the SiO_2 found is deducted from the weight of the BeO precipitate, and the total beryllium present in the sample is computed.

(b) Determination of Beryllium Oxide in Beryllium Metal. In determining the free beryllium in beryllium metal, the beryllium oxide in the metal is determined and is deducted from the total beryllium to give the amount of free beryllium. The beryllium metal is volatil-

ized with hydrogen chloride gas at a temperature of 600°C , and the beryllium in the residue is colorimetrically determined with *p*-nitrobenzeneazo-orcinol.

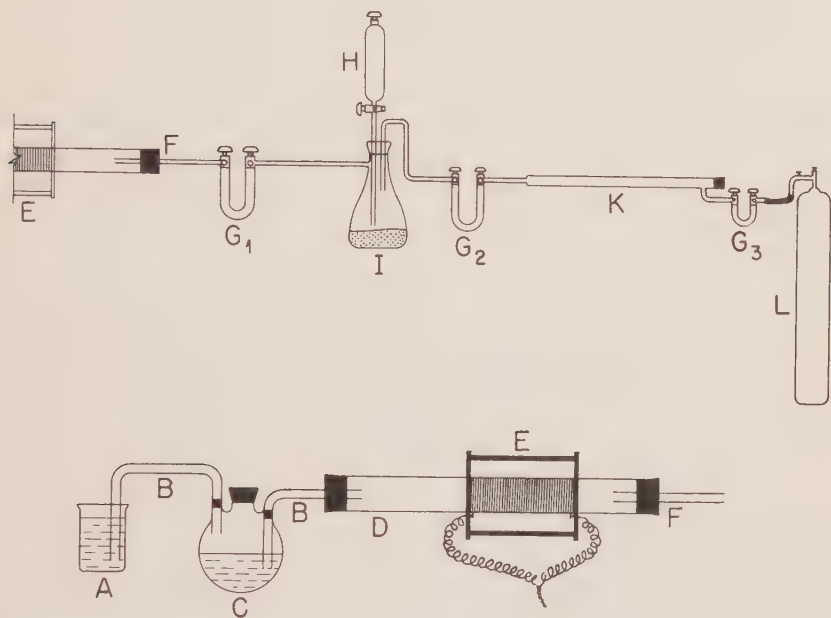


Fig. 11.1—Hydrogen chloride volatilization apparatus. A, 1-liter beaker containing strong sodium hydroxide solution; B, pyrex tubing, 1 cm bore; C, 500-ml distilling flask containing concentrated sulfuric acid; D, Vycor combustion tube, 25 by 31 by 750 mm; E, heating coil, chromel A wire, B & S gauge 18 (0.040 in. in diameter), 0.406 ohm per foot, 100 turns spaced approximately 1.5 mm apart on the Vycor tube; F, pyrex tubing, 4 mm bore; G_1 , G_2 , G_3 , 150-mm Schwartz drying tubes, phosphorus pentoxide; H, 250-ml cylindrical separatory funnel, glass stoppered and long stemmed, containing concentrated sulfuric acid; I, 500-ml filtering flask containing sodium chloride dried at 120°C ; K, quartz combustion tube, 520-mm long and 17 mm bore, with reduced end and side tube, containing copper turnings; L, helium tank.

Procedure.⁸ A 0.2-g sample of the metal is accurately weighed in a small platinum boat (2.5 by 0.5 by 0.5 in.). The sample is placed in the Vycor volatilization tube D (see Fig. 11.1), directly under the heating coil E. All connections are made airtight. The stopcocks on the drying tubes G_1 , G_2 , and G_3 are opened. Helium from tank L is passed through the system at a rate of one bubble per second at the outlet A. After 10 min a Meker burner is placed under K, which con-

tains copper turnings. The heating coil E is then turned on with a Variac adjusted to give a temperature of approximately 200°C . After 1 hr the helium rate is reduced to one bubble every 2 sec at the outlet A. The temperature inside D at E is raised to about 600°C . The stopcocks at G_2 and G_3 are turned off, and the stopcocks to the thistle tube H, which contains concentrated H_2SO_4 , are opened. The helium-tank valve is now entirely closed. Concentrated H_2SO_4 is allowed to react with NaCl in flask I (predried at 120°C) in order to give a steady, rapid flow of HCl gas. This rate can be judged by the bubbling in flask C. Beaker A contains a strong solution of NaOH, which absorbs the HCl gas and any BeCl_2 . Notice is taken of the time at which the last bubble of hydrogen issues from the outlet A, and the flow of HCl gas is maintained for 30 min more. Some gentle heating of flask I may be necessary to maintain this flow of HCl, but excessive heating must be avoided. When the reaction is completed, the rubber stopper in the Vycor tube D holding the glass tubing B is removed. Flask I is then removed, and its contents are washed out with water. The rubber stopper in the Vycor tube D holding the glass tubing F is removed, and the platinum boat is carefully withdrawn from this end of the Vycor tube. The residue in the platinum boat is carefully brushed into a 50-ml platinum dish. The dish is placed over a Meker burner, and the residue is carefully ignited to free it of any carbon. After the dish is cooled, the residue is moistened with 2 ml of H_2SO_4 . The dish is placed on a hot plate and fumed for about 1 min. After cooling, about 5 ml of water is carefully added. If all the residue is not in solution, the sample is reheated gently on a hot plate until solution of the residue is complete. The solution is transferred to a 500-ml volumetric flask, made to volume, and mixed thoroughly.

For analysis of the beryllium content, two 25-ml and one 50-ml aliquots are pipetted into 150-ml beakers (the aliquot should contain 10 to 100 γ of Be). To each sample a few crystals of NH_4Cl and 1 ml (5 mg) of aluminum solution [31 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ per 500 ml] are added. Concentrated NH_4OH is added dropwise until the first permanent precipitate of $\text{Al}(\text{OH})_3$ is formed, and then 3 drops are added in excess. The solution is placed on a hot plate, heated nearly to boiling, and then filtered through a 7-cm Whatman No. 42 filter paper. The hydroxide clinging to the sides of the beakers is washed back with about 15 ml of water, and the precipitate on the paper is washed with this water. This process of washing the precipitate is repeated. It is not necessary to transfer all the precipitate to the paper. After the filtration and washings are complete, the filter is carefully removed and opened, and the precipitate is washed back into the original beaker. Not over 30 ml of water should be required to remove the precipitate entirely from the paper. It is desirable to have good lighting

available in order to observe that all the precipitate is removed from the paper.

To each solution exactly 5.70 ml of 2N NaOH is added from a buret. The samples are transferred to a hot plate, carefully boiled down to about 15 ml, cooled to room temperature, and transferred to 50-ml volumetric flasks containing exactly 10 ml of 0.64N boric acid solution (39.6 g of boric acid per liter). About 15 ml of water is used for washing out each beaker, thus leaving room in the volumetric flask for the addition of 6.00 ml of 0.025 per cent *p*-nitrobenzeneazo-orcinol reagent (0.125 g is dissolved in 500 ml of 0.1N NaOH, and the solution is stirred for several hours and filtered through a Whatman No. 54 filter paper). After the addition of the reagent the sample is made to volume and thoroughly mixed. The solution is poured into a clean, dry 100-ml beaker and allowed to stand for 5 to 10 min. Any filter-paper fibers will settle to the bottom. The solution is then carefully decanted into a 20-mm cell, and the transmittancy is determined against a reagent blank at 520 m μ by using a Beckman spectrophotometer. The reagent blank is prepared by diluting 5.70 ml of 2N NaOH, 10 ml of 0.64N boric acid, and 6.00 ml of 0.025 per cent *p*-nitrobenzeneazo-orcinol reagent to 50 ml.

The amount of beryllium is obtained from a calibration curve prepared by developing the color in a series of standards containing 10, 20, 30, 40, 50, 60, 70, 80, 100, 120, and 140 γ of beryllium. A standard beryllium solution is prepared as follows: 1 g of beryllium oxide, dried at 120°C, is dissolved in 10 ml of H₂SO₄ and diluted to 1,000 ml; 27.74 ml of this solution is then drawn from a buret and diluted to 1,000 ml to give a solution containing 20 γ of Be per milliliter.

The calibration curve obtained (see Fig. 11.2) does not obey Beer's law. For higher concentrations the optical densities are lower than those which would be obtained if Beer's law were obeyed.

(c) Determination of Traces of Beryllium. Beryllium may be determined in uranium metal and uranium compounds by spectrographic methods. Fluorescence methods have also been employed for the determination of beryllium in uranium and in other materials. The colorimetric method using *p*-nitrobenzeneazo-orcinol has been used for the determination of beryllium oxide in beryllium, as described previously.

(1) Fluorometric Method with Quinizarin. White and Lowe⁴⁴ described the fluorescence of alkaline beryllium solutions with 1-amino-4-hydroxyanthraquinone. Fairhall et al.⁹ found that the fluorescence was proportional to the beryllium concentration in the range of 0.05 to 10 γ and that 1,4-dihydroxyanthraquinone (quinizarin) likewise produced fluorescence.

The fluorescence of alkaline beryllium solutions containing quinizarin has been studied in detail by Underwood et al.¹⁰ The pH, dye concentration, and many common ions were shown to influence the fluorescence of the complex. The fluorescence varied with the dye concentration, and for each beryllium concentration an optimum amount of dye gives the optimum fluorescence. The pH was found to

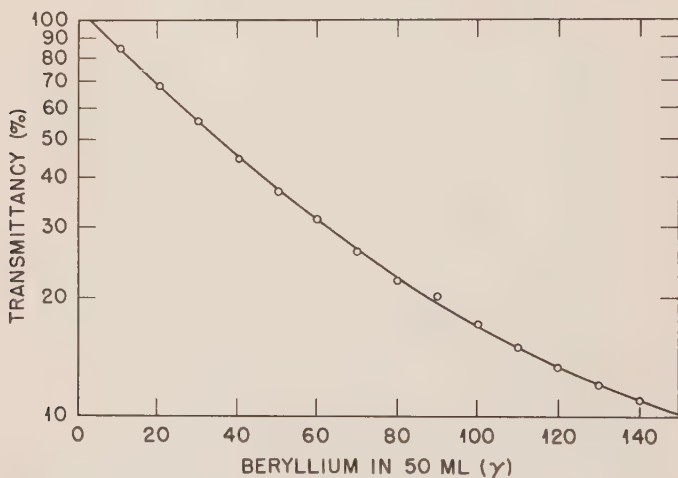


Fig. 11.2—Transmittancy-concentration curve for beryllium with *p*-nitrobenzeneazo-orcinol reagent.

be critical, as is shown in Fig. 11.3, with the maximum fluorescence occurring at a pH of 11.3 to 11.4. Sodium, phosphate, fluoride, bicarbonate, chloride, nitrate, and sulfate ions did not interfere with the fluorescence when they were present in the ratio of 1,000 parts to 1 part of beryllium. Calcium, magnesium, iron, copper, and manganese ions definitely interfered when present in the ratio of 10 to 1.

The procedure given below for pure beryllium solutions is by Underwood et al.¹⁰ for determining beryllium in the range of 1 to 10 γ per 20 ml, with an error of about 10 per cent.

Procedure.¹⁰ To the solution (less than 15 ml) containing 1 to 10 γ of beryllium are added 2 ml of 1N diethylamine (Eastman Kodak Co. grade, redistilled and dissolved in water), 0.3 ml of quinizarin solution (0.3 mg per milliliter of 95 per cent ethyl alcohol, the technical grade of quinizarin being sublimed and recrystallized from ethyl alcohol), and 4 ml of 0.1N HCl. The solution is then diluted to 20 ml, and the fluorescence is measured by means of a fluorophotometer

(Chap. 24 on "Photometric Methods"). A heat-resistant Corning ultraviolet filter No. 5874 is employed to reduce the visible light produced by the lamp, and a Corning No. 3486 filter is interposed between the sample chamber and the phototube to absorb ultraviolet radiation and transmit the orange-red fluorescence.

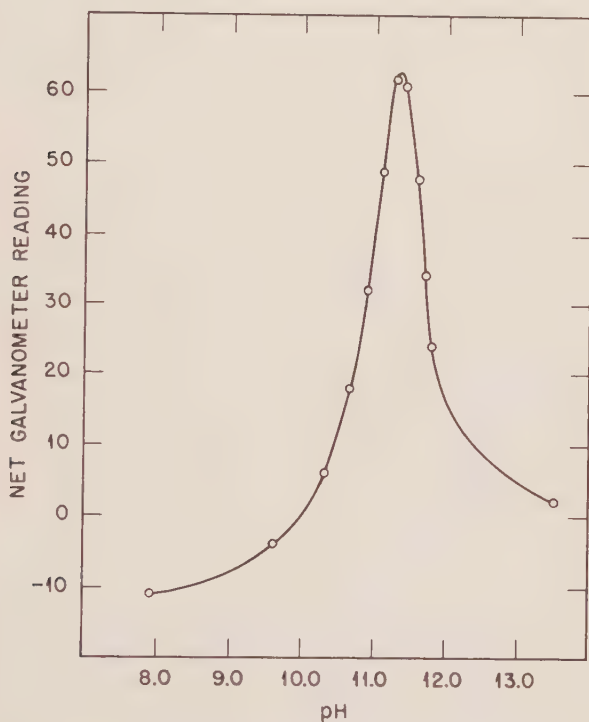


Fig. 11.3—Dependence of fluorescence of beryllium solution containing quinizarin on pH. Galvanometer deflections indicate degree of fluorescence.

The instrument is checked for stability and linearity of response by measuring the fluorescence of quinine sulfate solutions of various strengths, Corning No. 3385, 3389, and 4303 filters being used in place of the No. 3486.

The beryllium content is read from a standard curve obtained by treating known beryllium solutions in the same manner as mentioned above. A calibration curve is shown in Fig. 11.4.

(2) Fluorometric Method with Morin. Another method is based on the yellow-green fluorescence shown when beryllium in the presence

of morin in alkaline solution is irradiated by ultraviolet radiation.⁴ This method is based on the work of Zermatten.¹² Interferences such as calcium, scandium, and chromate are not likely to be present in the uranium compounds tested. Uranium is removed prior to the determination by extraction of uranium 1-nitroso-2-naphtholate with amyl alcohol. The recovery of beryllium by this method is 50 per cent. With the instrument used, a Spekker fluorometer No. 6553, the range is 0.1 to 8 γ .

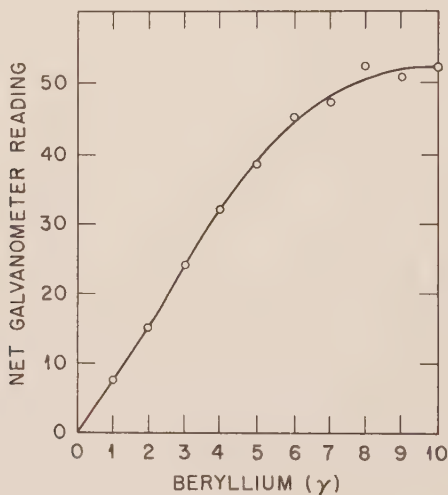


Fig. 11.4—Fluorescence-concentration curve for beryllium solution containing quinizarin. Galvanometer deflections indicate degree of fluorescence.

Procedure.⁴ A 2-g sample of uranium metal or oxide is dissolved with 10 ml of warm HNO_3 (1 to 4) and 1 ml of HCl . The solution is cooled, diluted to about 50 ml, and neutralized with NH_4OH , which is added dropwise with stirring until a very slight permanent precipitate has formed. Two drops of HNO_3 are added, and the solution is transferred to a 200-ml separatory funnel. A solution of 2 g of 1-nitroso-2-naphtholate in 10 ml of ethyl alcohol is added, and the solution is shaken. Two drops of NH_4OH are added, and the shaking is continued. The uranium 1-nitroso-2-naphtholate is extracted with two 25-ml portions of amyl alcohol, and the extracts are discarded. Another 0.2-g portion of 1-nitroso-2-naphtholate (dissolved in 5 ml of ethyl alcohol) is added, and the solution is shaken and extracted about five times with gradually diminishing quantities of amyl alcohol (20, 15, 10, 10, and 10 ml), the extracts being discarded. The aqueous so-

lution is transferred to a beaker, and the dissolved amyl alcohol is boiled off. The last traces of uranium are precipitated by adding 5 ml of 1N NaOH to the boiling solution (40 ml) and then filtering through a Whatman No. 40 filter paper into a 50-ml stoppered, graduated cylinder. The solution is cooled, made up to 50 ml with water, and mixed. Now 1.5 ml of a 0.004 per cent solution of morin (in methanol) is added, and again the solution is mixed.

The fluorescence of the solution is measured, and the beryllium content is obtained from a curve made from known amounts of beryllium carried through the procedure.

2. MAGNESIUM

Macro and micro amounts of magnesium were determined in many materials. Uranium and its compounds were analyzed for traces chiefly by spectrographic methods, as described in Chap. 26.

2.1 Methods of Solution. Magnesium is readily dissolved in dilute acids. The chief difficulty is the extreme violence of the reaction with acids, which is likely to cause a loss of material. Generally the sample is placed in water, and dilute acid is added in small amounts.

Magnesia is difficult to dissolve after ignition at high temperatures, but it may be sintered with sodium carbonate and then dissolved in perchloric or other acids.² Burned magnesite is dissolved with perchloric acid.²

Uranium metal and oxides are readily dissolved in nitric acid. Uranium tetrafluoride may be ignited to U_3O_8 and then dissolved in nitric acid.

2.2 Methods of Separation. In standard methods of analysis^{1,2} nearly all the other metals of the periodic table with the exception of the alkalis are removed before the determination of magnesium. This was generally found to be necessary in the analysis of uranium and thorium. Johnston and Larson¹³ used hydrogen peroxide to separate the bulk of the uranium from magnesium with a 95 per cent recovery of the magnesium.

Procedure.¹³ A sample of metal or oxide is dissolved in HNO_3 . The pH is adjusted as follows: 4N NH_4OH is added until a small amount of ammonium uranate remains, and then a few drops of 2N HNO_3 are added until the solution is clear. Peruranic acid is precipitated by adding 5 ml of 30 per cent H_2O_2 per 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$. The mixture is filtered through a Whatman No. 40 filter paper, and the filtrate is evaporated to dryness to destroy excess peroxide.

The residue is dissolved in dilute HCl and transferred to a 250-ml Erlenmeyer flask. Five grams of NH_4Cl per 200 ml and 1 drop of methyl red are added. The solution is neutralized with 6N NH_4OH by

adding 2 ml of NH_4OH per 100 ml in excess. The solution is then cooled, saturated with H_2S , stoppered with a clean cork, and cooled in a refrigerator for 2 hr. It is then filtered and washed with cool 2 per cent NH_4Cl containing a little $(\text{NH}_4)_2\text{S}$.

The filtrate, which contains calcium and magnesium, is boiled to remove H_2S and made slightly acid with 1N HCl , and the boiling is continued. (If necessary, it is filtered through a Whatman No. 42 filter paper to remove the sulfur.) It is rendered ammoniacal with 6N NH_4OH and heated to boiling, and a hot 4 per cent solution of ammonium oxalate (25 ml per 75 ml of solution) is added slowly with stirring. It is boiled for 1 to 2 min and heated on a steam bath for 30 min. Next it is cooled and allowed to stand for 2 hr, after which it is filtered and washed with five 10-ml portions of cold 0.1 per cent ammonium oxalate. The filtrate is used for the magnesium determination.

Short¹⁴ used an ether separation of the nitrate and removed the remaining uranium with ammonium hydroxide. It was found necessary to make a double precipitation with ammonium hydroxide, because 30 to 50 per cent of the magnesium was occluded in a single precipitation. Heavy metals were removed by hydrogen sulfide. A single ammonium hydroxide precipitation has been used to separate the uranium,¹⁵ but in view of the work of Short complete recovery of the magnesium is doubtful.

The usual separation methods,^{1,2} whereby silica, the hydrogen sulfide group of metals, the ammonium hydroxide group, and calcium are removed prior to a gravimetric determination, were used to some extent with commercial U_3O_8 .

Attempts to separate traces of magnesium from ammonium carbonate solution with 8-hydroxyquinoline or with sodium carbonate were not successful.¹⁴

2.3 Methods of Determination. (a) Gravimetric Methods. Gravimetric methods were used only for the relatively large amounts of magnesium. For traces of magnesium colorimetric methods were used. The conventional methods of analysis, whereby magnesium is precipitated as the phosphate,^{1,2} were employed for the analysis of crude U_3O_8 .^{13, 16, 17}

The total magnesium in magnesium metal has been analyzed by precipitating with 8-hydroxyquinoline and drying the resulting 8-hydroxyquinolate.¹⁸ Not enough interfering elements were present to affect the results seriously. This method^{19, 20} has also been used for the analysis of commercial U_3O_8 after interfering substances have been removed.

Procedure.¹⁸ A 1-g sample is weighed and transferred to a 250-ml Erlenmeyer flask. To this are added 25 ml of H_2O and then, carefully

and in small portions, 40 ml of dilute HCl. The mouth of the flask is kept covered with a small watch glass when acid is not being added. The flask is placed on the steam bath until all the metallic particles have dissolved and effervescence has ceased. The solution is cooled, then transferred to a 1-liter volumetric flask, diluted to volume, and mixed well.

A 25-ml portion of the sample solution (0.025-g sample) is transferred to a 150-ml beaker. A 1-g sample of NH_4Cl , 10 ml of NH_4OH , and 15 ml of H_2O are added, and the solution is heated nearly to boiling. With stirring, 15 to 20 ml of 8-hydroxyquinoline solution is added (2 g of reagent in a mixture of 6 ml of glacial acetic acid and 95 ml of water). After the reagent is added, the solution should be a rather deep-yellow color, indicating an excess of the reagent. It is then covered with a watch glass, heated to boiling, and left on the steam bath for 15 min with intermittent stirring. The precipitate is filtered onto a sintered-glass crucible of medium porosity (previously dried at 100 to 105°C) and then is weighed. The precipitate is washed with 100 ml of hot dilute NH_4OH , dried at $105 \pm 1^\circ\text{C}$ for 1 hr, weighed, and dried to constant weight.

(b) Volumetric Method. The volumetric method, whereby magnesium 8-hydroxyquinolate is dissolved in hydrochloric acid and oxidized with bromine water, and the liberated iodine is titrated with sodium thiosulfate after the addition of potassium iodide,¹⁹ has been employed.¹⁸

Procedure.¹⁸ The magnesium is precipitated as the hydroxyquinolate, as described under the gravimetric procedure. The precipitate is filtered onto a Whatman No. 40 filter paper, and the precipitate adhering to the beaker is washed onto the filter. The precipitate on the filter is then washed with three 25-ml portions of hot dilute NH_4OH . The filtrate is discarded, and the precipitate is dissolved by washing the filter with 25 ml of warm dilute HCl. The filter paper is then washed with 50 ml of water, and both the filtrate and the washings are collected in a 1-liter Erlenmeyer flask. To the solution are added 170 ml of water and 80 ml of HCl. It is then cooled, and 1 ml of methyl red indicator is added. The solution is titrated slowly with 0.2N Br_2 solution until the indicator just changes to yellow. Three grams of KI is added, and the liberated I_2 is titrated with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ with the use of a starch indicator.

(c) Gasometric Method. Free magnesium in magnesium metal has been determined by the measurement of the hydrogen gas evolved when the sample is treated with an acid.²¹ The method is similar to the one used for the determination of zinc in zinc dust.² The sample is dissolved in hydrochloric acid, and the gas evolved is measured in a gas buret with a 2-liter bulb instead of the usual 250-ml bulb.

(d) Colorimetric Method. When magnesium hydroxide is precipitated by sodium hydroxide in the presence of titan yellow, a red or orange-red lake is formed, which remains dispersed for 8 hr or longer. The color is more intense in the presence of calcium ion, which is introduced in the form of a saturated calcium sulfate solution.²² The method has been applied to the determination of magnesium in uranium after removing the uranium.¹⁵ From 50 to 600 γ of magnesium can be detected by this method with an accuracy of about 20 per cent. Aluminum, arsenic, beryllium, bismuth, cadmium, cobalt, lanthanum, manganese, nickel, tin, and zinc interfere, but they were not present in sufficient amounts in the materials examined. In one method¹⁴ based on the above principle, interfering elements are removed, and chlorazol brilliant yellow 3 G. S. is used as a reagent to form the lake.

Procedure.¹⁵ A 10-g sample of uranium metal is dissolved in 25 ml of HNO_3 (1 to 1), and the solution is evaporated to dryness. The nitrate is taken up with redistilled water, and a few drops of HNO_3 (1 to 1) are added, if necessary, to clear the solution. The solution is then transferred to a 50-ml volumetric flask and made to volume. Two 10-ml aliquots are taken and then transferred to 200-ml centrifuge bottles. Approximately 70 ml of 1.5 per cent NH_4Cl solution and 6 ml of 4N NH_4OH are added to this solution with constant stirring. The solution is then centrifuged for 10 min at 2,000 rpm. If the solution is not clear, a few drops more of 4N NH_4OH are added to complete the precipitation of the uranium, but care is taken to keep the concentration of NH_4OH as low as possible. Generally 6 ml of 4N NH_4OH is sufficient to precipitate the uranium in a 2-g sample.

The clear solution is decanted through a Whatman No. 40 filter paper into a 400-ml beaker. Approximately 15 ml of the 1 per cent NH_4OH solution and 15 ml of the 1.5 per cent NH_4Cl solution are added to the centrifuge bottle. The solution is well stirred with a glass stirring rod and centrifuged, and the clear solution is decanted through the filter. This washing procedure is repeated twice so that the precipitate receives a total of three washings. The combined filtrates are evaporated to dryness, and the sides of the beaker are heated with an open flame to remove all ammonium salts that collect thereon.

To the dried residue 1 ml of 1N H_2SO_4 is added, and the acid solution is allowed to come in contact with the entire bottom surface of the beaker. The sides of the beaker are washed down with the 0.2N HNO_3 wash solution, and the solution is transferred to a 100-ml volumetric flask; the volume is kept at less than 50 ml, because the added colorimetric agents total 50 ml. The following are added in order:

10 ml of 1.0 per cent starch solution (prepared freshly every three or four days); 20 ml of saturated CaSO_4 solution; 10 ml of 0.05 per cent titan yellow solution; and 10 ml of 2N NaOH solution.

The solution is diluted to the mark with redistilled water, and the contents are transferred to a 250-ml glass-stoppered Erlenmeyer flask. A blank should be prepared by using the colorimetric reagents, beginning with the 1 ml of 1N H_2SO_4 , and using redistilled water for dilution. All the solutions are shaken vigorously for 10 min (with a suitable mechanical shaker), and then a portion of each solution is transferred to a spectrophotometer cuvette. The transmittancy is read at 530 $\text{m}\mu$.

3. CALCIUM

The determination of calcium in uranium metal was of interest. Commercial uranium oxide and some ores were analyzed by conventional methods. For the determination of traces of calcium in uranium-base material the spectrographic method (Chap. 26 on "Spectrochemical Methods") was found to be more satisfactory than chemical methods.

3.1 Methods of Solution. Calcium metal reacts vigorously with acids. It was therefore found more satisfactory to have the calcium react with water prior to the addition of the acid. Uranium and most of its compounds were readily soluble in nitric acid. Uranium tetrafluoride was ignited to U_3O_8 prior to solution. It may also be fused with boric acid to effect solution.

3.2 Methods of Separation. The conventional scheme of analysis^{1,2} —whereby silica is removed by dehydration, the heavy metals are precipitated with hydrogen sulfide, and the ammonium hydroxide group is removed—was followed for the separation of calcium in the analysis of commercial U_3O_8 , ores, and solutions (see references 20, 23-25, 42). Hydrogen peroxide has been used to remove the uranium prior to a calcium determination.²⁶ The procedure for the uranium separation is given above under magnesium. The extraction of uranyl nitrate with ether, followed by a carbonate precipitation, has been used for the same purpose.²⁷ A separation based on the insolubility of calcium sulfate in alcohol¹ has also been employed.²⁸ A discussion of methods for the separation of uranium from calcium is given by Warf.²⁹ From this work the peroxide precipitation and the ether extraction of the nitrate appear to be the more promising.

Sulfosalicylic acid has been used³⁰ to complex thorium before precipitating calcium as the oxalate from a solution containing excess ammonium sulfosalicylate.

3.3 Methods of Determination. The conventional method,^{1,2} whereby calcium is precipitated as the oxalate and then ignited to CaO, or titrated with permanganate or ceric sulfate, has been used extensively (see references 20, 23, 24, 27, 28, 30-32).

An indirect colorimetric method has been employed by Warf²⁹ for the determination of calcium in uranium metal.

(a) Gravimetric Method. The precipitation of calcium as calcium oxalate, followed by ignition to calcium oxide (adequately covered in standard reference works), was used in the analysis of ores.

(b) Volumetric Methods. Titration of calcium oxalate by permanganate or ceric sulfate is described in standard reference works.^{1,2,33} The procedures given below illustrate the separation from thorium and uranium.

(1) Procedure in the Presence of Thorium.³⁰ A sample containing 0.02 to 0.1 g of calcium is treated with 2 to 5 g of sulfosalicylic acid and neutralized to methyl red with ammonium hydroxide. (No precipitation should occur at this stage. If a precipitate does appear, 2 g more of sulfosalicylic acid is added to the solution, and the solution is again neutralized with ammonium hydroxide.) Just enough acetic acid to make the solution acid to methyl red is then added, and the solution is diluted to 200 ml and heated to boiling. A 25-ml quantity of 4 per cent ammonium oxalate is added while the solution is still hot, and the solution is digested below the boiling point. The solution is neutralized by the dropwise addition of ammonium hydroxide and digested for 1 hr. The solution is cooled and filtered, and the precipitate is washed with water. The calcium oxalate is dissolved from the paper back into the original beaker with H₂SO₄ (1 to 12). Excess standard ceric sulfate is added, and the solution is heated above 50°C and allowed to cool to room temperature. The excess ceric sulfate is titrated with ferrous ammonium sulfate, with the use of 0.025N ferroin as indicator. The solution progresses from yellow through green and blue to a final red at the end point. (If this procedure is employed for determining a trace of calcium in thorium nitrate, two precipitations may be necessary.)

(2) Procedure in the Presence of Uranium.²⁷ A 10-g sample of uranium metal is dissolved in HNO₃ (1 to 1), and any insoluble matter is filtered off. The filtrate is evaporated until crystallization occurs, and it is stirred thoroughly during cooling to prevent the mass from caking. The crystals are dissolved in 60 ml of ether and transferred to a separatory funnel with an additional 20 ml of ether, any insoluble matter being retained in the beaker. The ether layer is extracted with three small portions of water. The aqueous layers are run into the beaker containing the insoluble matter. The ether is evaporated

on a water bath, and, if there is any insoluble matter, a small amount of nitric acid is added and warmed until solution is complete. By means of a standard iron solution 1 mg of iron is added to act as a carrier in the subsequent precipitation. In the case of impure samples this addition is unnecessary.

In another beaker 5 g of sodium carbonate is dissolved in 100 ml of water. This solution is boiled, and the aqueous layers from the ether separation are carefully added and boiled gently for at least 45 min. It is cooled and filtered on a 7-cm Whatman No. 40 filter paper; then it is washed three times with 5 per cent sodium carbonate solution (recently boiled) and once, finally, with a small amount of water.

The precipitate is dissolved and washed into the original beaker with hot 10 per cent HCl. It is then transferred to a 50-ml beaker and evaporated to about 5 ml volume. A 4-ml sample of 4 per cent ammonium oxalate, 1 drop of bromphenol blue (0.04 per cent in dilute alcohol), and ammonium hydroxide (1 to 10) are added until the solution is just blue in color. The solution is boiled and allowed to stand at least 1 hr. It is then filtered through a 7-cm Whatman No. 40 filter paper and washed six times with oxalic acid solution (6 mg per liter). The precipitate is dissolved through the filter with hot sulfuric acid (1 to 10), and the solution is heated to 75°C and titrated with 0.1N permanganate. (For a more accurate end point 0.01N ceric sulfate may be used with 1,10-phenanthroline ferrous indicator.) A blank is carried through the entire procedure.

(c) Colorimetric Method. A colorimetric method based on the work of Jendrassik and Takacs³⁴ has been modified by Warf²⁹ for the determination of calcium in uranium metal. After separation from the uranium the calcium is precipitated as the oxalate. This is dissolved in hydrochloric acid, and a measured amount of ferric chloride (in excess) is added in the dark. Sulfosalicylic acid is then added. The $\text{C}_2\text{O}_4^{--}$ and Fe^{+3} form a complex; then the excess Fe^{+3} and the sulfosalicylic acid form a violet-colored substance. The measurement of the intensity of this color reveals how much Fe^{+3} is in excess; the greater the amount of oxalate, the less intense is the color. Jendrassik and Takacs state that light causes the oxidation of $\text{C}_2\text{O}_4^{--}$ by Fe^{+3} ; the addition of sulfosalicylic acid, however, renders the solution stable to light.

(1) Reagents.²⁹ Two standard iron solutions were made, one for small amounts of calcium and one for larger amounts. A stock solution of FeCl_3 solution was made by dissolving 6.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 10 ml of HCl and diluting to 100 ml with water. The standard FeCl_3 for less than 200 γ of calcium is prepared by diluting 10 ml of the stock solution to 500 ml; the standard FeCl_3 for more than 300 γ of

calcium is prepared by diluting 20 ml of the stock solution to 500 ml. The standard $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution is made by dissolving 7.0 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in water and diluting to exactly 1 liter. One milliliter of this solution is then equivalent to 2 mg of calcium.

(2) Procedure.²⁹ To 1 ml of the sample solution in a 15-ml centrifuge tube 1 ml of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution is added. One milliliter of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ should be used for each milligram of calcium present. The solution is colored with very dilute methyl red, and 3N NH_4OH is added until the yellow color appears; then about 0.5 ml is added in excess. The tubes are placed in boiling water for 30 min and then centrifuged. After decantation the precipitates are washed three times with approximately 3 ml of alcohol-ether-water mixture (6 to 6 to 5), once with 3 ml of alcohol-ether mixture (1 to 1), and once with 3 ml of ether. The precipitates are stirred with a drawn-out glass rod during all the washings except the last, with centrifuging between each washing. The ether from the last washing is expelled by warming in an oven for a few minutes.

One milliliter of 0.5N HCl is pipetted into each tube, and the tubes are again heated in boiling water until complete solution is obtained. As each tube is used, its contents are rinsed into the cuvette (test tube marked at 7 ml) by using a fine jet of water (about 3 ml of wash water). The cuvette is placed in a blackened tube, and 1 ml of FeCl_3 reagent is added from a pipet, followed by 2 drops of saturated $\text{KH}(\text{IO}_3)_2$ and 1 ml of 0.16N sulfosalicylic acid. After stirring, the solution is made to volume and the transmittancy is measured against water.

The method has not been investigated thoroughly for interference. It is applicable only when calcium has been separated from other elements.

4. STRONTIUM AND BARIUM

The determination of strontium and barium was made in the majority of cases by spectrographic methods, as described in Chap. 26 on "Spectrochemical Methods." Macro amounts of barium were determined by the conventional sulfate precipitation.^{1,2} Separation of these elements for spectrographic or radiometric analysis was the only development work done.

Methods of Separation. Some workers²⁷ have used the carbonate separation, as given above under calcium, for the separation from uranium prior to spectrographic analysis.

A method based on the insolubility of barium and strontium nitrates in fuming nitric acid³⁵ has been employed to separate these elements prior to radiometric analysis.³⁶ Normal barium and strontium nitrates

are added as carriers. Barium is removed from strontium as the chromate in buffered (pH 5) acetate solution.³⁷

5. RADIUM

The analysis of ores and concentrates for their radium content was an essential part of the raw-materials analytical program. An important part of the determination of this element is the solution of the sample, since a radioactive substance must be dissolved or fused in order to liberate radon from it. The radon emanation method was used for the determination; it is described in detail in this chapter because it is not one of the general methods of radiometric analysis that are given in Chap. 28 on "Radiochemical Analytical Methods." A résumé of standard methods for the determination of radium is given by Lind.³⁸

5.1 Methods of Solution. The material analyzed for radium was generally of two types. In the first, the radium was present in raw ores; in the second, the radium was present in sludges containing considerable lead and barium sulfate.

(a) **Ores.** Pitchblende is readily soluble in nitric acid, and this method has been used extensively for this type of material. The insoluble residue remaining has been checked for radium and has been found to be of the order of 10^{-12} g per gram of sample. The residue may be fused with sodium carbonate and then treated with nitric acid if necessary. The same treatment has been used on carnotite ore, but in this case the silica remaining after the acid treatment is volatilized with hydrofluoric acid, the insoluble residue is fused with sodium carbonate, and the melt is dissolved in nitric acid.

Procedure with Pitchblende Ores.³⁹ A 1-g sample of ore is weighed into a beaker and wet with water. After 50 ml of HNO_3 (1 to 1) has been added, the mixture is covered with a watch glass and heated just below boiling for at least 1 hr. The solution is diluted to 75 ml with water and filtered through a Whatman No. 42 filter paper into a 1-liter volumetric flask. The insoluble residue is washed thoroughly with warm water.

The filter paper and the residue are ignited in a 25-ml platinum crucible. To the residue is added a little water and 20 ml of HF, and the solution is evaporated to dryness on a hot plate. The residue is fused for 1 hr with 8 g of sodium carbonate, and the melt is cooled and dissolved in dilute HNO_3 , the solution being added to the filtrate in the volumetric flask.

In another procedure,⁴⁰ a 50- to 100-ml sample is treated with 3 ml of 60 per cent HClO_4 and 10 ml of HF in a platinum crucible. This is evaporated to fumes of HClO_4 on a hot plate. An additional 10 ml of

HF is added, and the solution is again brought to fumes. With high-grade ores three evaporations with HF are used; with medium-grade ores, four evaporations; with low-grade ores, five evaporations. The residue in the crucible is then taken up with 100 ml of 1 per cent nitric acid, and the solution is used for the radium determination.

(b) Sludges Containing Lead and Barium. The fusion of radium-bearing sludges with potassium pyrosulfate³⁸ was found to give erratic results. The method that was used to the greatest extent consisted of removing the silica with hydrofluoric acid, fusing the residue with sodium carbonate, and dissolving the melt in nitric acid.

Procedure.³⁹ A 0.2000-g portion of the ground sample is placed in a 100-ml platinum dish and moistened with water. Then 20 ml of nitric acid (1 to 1), 10 ml of 70 per cent perchloric acid, and 20 ml of hydrofluoric acid are added. The dish and contents are heated on a hot plate to dryness.

A 20-g sample of ammonium acetate and 5 ml of water are added and mixed with the dry residue. The dish is covered and allowed to digest on the steam bath for 15 min; then 15 ml of nitric acid and 10 ml of water are added. After standing for 10 to 15 min the mixture in the dish is stirred and filtered through a Whatman No. 42 filter paper into a 1-liter volumetric flask. The paper and insoluble residue are washed thoroughly with water.

The filter paper and contents are transferred to a platinum crucible and ignited until all the paper is ashed. The residue is fused with sodium carbonate for 30 to 60 min. After cooling, the crucible and contents are placed in a 600-ml beaker; then 400 ml of water and 60 ml of HNO_3 are added. After the sample is completely in solution, it is transferred to the 1-liter flask containing the first filtrate. After making up to volume and measuring, a 50-ml aliquot is used for the radium analysis.

5.2 Methods of Determination. For the determination of radium the emanation method³⁸ or the modified method of Curtiss and Davis⁴¹ found application.

In the latter method, the solution containing the radium is de-emanated, and the radon is allowed to build up over a certain period of time. The radon is then transferred to an ion-counting chamber. The amount of radon is determined by counting the alpha particles. A linear amplifier, scaling circuit, and traffic recorder are used to register the counts.

Procedure.⁴¹ The amount of solution used is 100 to 200 ml, containing roughly 10^{-9} g of radium. If necessary, however, solutions containing as much as 10^{-8} g of radium or as little as 10^{-13} g can be measured.

The solution is placed in flask S (see Fig. 11.5), fitted with a reflux condenser, and de-emanated by boiling at a reduced pressure of approximately 0.5 atm, while nitrogen is bubbled through it, usually for 17 or 18 min. The flask is then sealed off by stopcocks T_1 and T_2 , at atmospheric pressure, and the radon is allowed to collect until it is

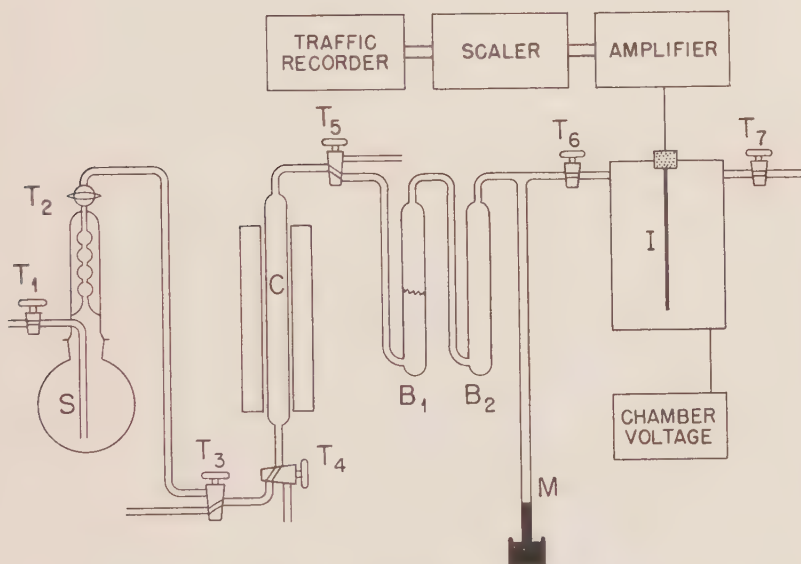


Fig. 11.5—Schematic diagram showing separation and determination of radon. S, standard radium solution; C, reduced copper; B_1 , Drierite; B_2 , P_2O_5 ; M, open mercury manometer; I, ion-counting chamber; T_1 to T_7 , stopcocks.

transferred to the chamber. The usual collection time that is convenient is of the order of one day. The amount of radon in curies collected is equal to $(1 - e^{-\lambda t})M_{Ra}$, where M_{Ra} is the amount of radium in solution in grams, t is the time of collection in hours, and $\lambda = 0.00755$. The longer the collection time (up to a practical limit of about thirty days), the more radon is collected per gram of radium. In measuring small quantities a longer collection time would be an advantage.

The transfer of the radon is accomplished by reboiling in the same manner as above and allowing the nitrogen containing the radon to flow into the evacuated ion chamber. The nitrogen is purified by passing through hot reduced copper, C, to remove oxygen; through Drierite

(B₁) and P₂O₅ (B₂) to remove water vapor; and through Ascarite (B₁) to remove CO₂.

The radon is allowed to come to equilibrium in the chamber for at least 3 hr. The count is usually made for 12 hr during the night, when vibrations and voltage fluctuations of power lines are less prominent.

The calculations consist in determining the average count per hour above background and dividing by $K(1 - e^{-\lambda t})e^{-\lambda T}$, where K is the calibration count per hour per curie, determined by running a standard radium solution containing 10⁻⁹ g of radium; $\lambda = 0.00755$ per hour; t is the collection time in hours; and T is the decay time in hours, which is the interval between the transfer of the radon to the chamber and the beginning of the 12-hr record. If the calibration count is made for the same period, in this instance 12 hr, no additional correction is necessary.

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Chapter 12

GERMANIUM, TIN, AND LEAD

By R. E. Telford and N. H. Furman

The analysis of materials for these elements was for the most part limited to the determination of minor amounts of lead in a great variety of materials. Occasional determinations of germanium and tin were necessary in certain alloys or for other purposes.

1. GERMANIUM

Germanium is likely to be encountered in the form of the element or its alloys or in germanium(IV) compounds. Bivalent germanium is readily oxidized in solution and is not found in solutions that have been exposed to air or various oxidants. The volatile tetrachloride, the dioxide, and the disulfide are the most important compounds for analytical purposes. The sulfide dissolves in alkali sulfides with the formation of thiogermanates.¹

1.1 Methods of Solution. The metal and its alloys are best dissolved by a nitric-sulfuric acid mixture. Halogen acids, especially hydrochloric, are not used unless provision is made to trap the volatile halide in alkali. Germanium itself is dissolved or rapidly attacked by molten alkalis, sodium carbonate, molten potassium nitrate, and potassium chlorate.² Minerals are attacked by fusion with a sixfold quantity of a mixture of sulfur and sodium carbonate (1 to 1); the germanium forms a soluble sulfo salt that may be extracted by water.³ Germanium and certain of its alloys attack platinum crucibles.

1.2 Methods of Separation. The best method for separating germanium from complex mixtures is by distillation of the tetrachloride from a concentrated hydrochloric acid solution in a closed system provided with a condenser. If a distilling column is used, germanium may be separated in pure form when chlorine is added to oxidize arsenic.⁴

Germanium is a member of the alkaline sulfide group. Its disulfide is unusual because precipitation is complete only when a rather high concentration of acid is present; 6N sulfuric acid is a suitable concentration.⁵

Germanium, like tin, is complexed by fluoride or oxalate in acidic solutions; hence trivalent arsenic and antimony and many other metals of the hydrogen sulfide group may be separated by precipitation with hydrogen sulfide. The germanium and tin remain in the filtrate.⁶

It is possible to separate 1 γ of germanium from 1 g of uranium by distillation from 5N HCl and precipitation with hydrogen sulfide, using kieselguhr as a carrier. The precipitate is centrifuged and washed with hydrogen sulfide water. The suspension of the precipitate in water is placed on a graphite electrode, and the germanium is estimated spectrographically.⁷

1.3 Methods of Determination. Germanium sulfide may be converted to the dioxide by oxidation with ammonia and hydrogen peroxide.⁸ Oxidation with nitric acid is less satisfactory. Hydrolysis with water is also recommended.⁹ The final ignition temperature is 900 to 1000°C.

Germanium may be recovered from slightly acidic solution by precipitation with tannin and then igniting the precipitate to the oxide. This method has been applied to ferro alloys¹⁰ after distillation of the germanium as the chloride, and it has also been applied to aluminum-silicon alloys.¹¹ Arsenic in moderate amounts does not interfere.

Magnesium orthogermanate, Mg_2GeO_4 , has been recommended as a weighing form.¹² Phosphate and arsenate are precipitated under the same conditions, i.e., slightly ammoniacal solution.

The 8-hydroxyquinolate of germanomolybdic acid has been recommended for recovery of germanium from solution.^{13,14}

The reduction of germanomolybdic acid by ferrous solution gives a blue solution that has been used for the colorimetric estimation of germanium in the range 5 to 25 γ of germanium per 25 ml. Arsenic, silica, and phosphate interfere and must be separated.¹⁵ The range of the methods used is given in Table 12.1.

Analysis of Aluminum-Silicon-Germanium Alloys. Germanium is distilled as the tetrachloride, precipitated with tannin, and weighed as GeO_2 .^{10,11} The use of chlorine prevents the distillation of arsenic under the conditions that are used. Moderate amounts of arsenic do not interfere with the precipitation by tannin. Distillation of tin is prevented by the presence of sulfuric acid. Fifty milligrams is an optimum amount of germanium, and an accuracy of 0.5 mg is obtained with a precision of ± 0.2 mg.

Procedure.¹¹ Samples of a size that would contain about 50 mg of germanium are weighed. The sample is placed in a distilling flask provided with chlorine inlet, separatory funnel, and condenser. The condenser outlet is immersed in 100 ml of distilled water that is cooled in an ice bath. Twenty to thirty milliliters of acid mixture (485 ml of water plus 115 ml of sulfuric acid, and 200 ml of nitric acid) is added. Air is allowed to bubble through at a rate just suffi-

Table 12.1—Range of Methods

Method	Range
Gravimetric, tannate	10–50 mg
Spectrographic, carrier-distillation	0.2 ppm

cient to maintain a positive pressure. The flask is heated gently until the sample is dissolved. Thirty milliliters of hydrochloric acid is added through the separatory funnel, and distillation is continued for 30 min. Two grams of hydroxylamine hydrochloride is added to the distillate to reduce oxidizing substances, and then about 30 ml of freshly prepared 5 per cent tannin solution is added slowly with stirring. Ammonium hydroxide is added to the methyl red point; then 10 drops of sulfuric acid are added. The acidity may be as high as 1N.¹⁶ The contents of the beaker are heated to incipient boiling, and the precipitate is then allowed to settle.

Any insoluble material in the still is filtered, washed with water, ignited, and fused with a few grams of sodium carbonate. The melt is transferred into the still after it has been dissolved in sulfuric acid (1 to 3). Thirty milliliters of hydrochloric acid is added, and the distillation and tannin precipitation are repeated. The precipitates are filtered on a Whatman No. 40 15-cm filter paper and washed free of chloride with a wash solution of 50 g of NH_4NO_3 , 5 g of tannin, and 5 ml of HNO_3 per liter of solution. Chloride must be completely washed out to avoid loss during the final ignition. The precipitate is dried and ignited in a weighed platinum crucible at 600°C for 1 hr. The crucible is cooled, 5 drops of H_2SO_4 and 3 ml of HNO_3 are added, the acids are carefully expelled, and the carbon is burned off completely. The crucible is finally heated to 900 to 1000°C for 10 min. Results will be too high if the temperature is below 900°C and too low if the temperature is above 1000°C . After cooling the germanium is weighed in the form of GeO_2 .

2. TIN

Macro determinations of tin were of minor importance. Estimations were made by the conventional gravimetric methods based upon the precipitation of metastannic acid, stannic cupferrate, or of stannic sulfide followed by ignition to stannic oxide. Titration of stannous solutions with iodine or with other oxidants is frequently preferable to the gravimetric methods. The colorimetric determination with dithiol was useful.

2.1 Methods of Solution. Oxidized products containing tin are dissolved either upon alkaline fusion attack or upon reduction followed by acid treatment. The well-known nitric acid attack on alloys yields metastannic acid admixed with various other elements such as antimony, iron, and phosphate. Alloys dissolve in mixtures of nitric acid and various complexing agents such as oxalic or tartaric acids¹⁷ or nitric and hydrofluoric acids.¹⁸ Alloys are dissolved by concentrated sulfuric acid, but lead sulfate from alloys high in lead may make the process inefficient.¹⁹ Hydrochloric acid with the addition of an oxidant such as bromine, potassium chlorate, or nitric acid dissolves various alloys. Loss of stannic chloride may occur if a solution of stannic chloride plus free hydrochloric acid is evaporated. When sulfuric acid is present the loss does not occur.²⁰

2.2 Methods of Separation. Tin is separated with the hydrogen sulfide group in dilute hydrochloric acid (2.5 ml of HCl in 140 ml of solution). The tin is separated from mercury, lead, bismuth, copper, and cadmium by extracting the sulfides with ammonium sulfide to form soluble sulfo salts of tin.¹⁹ A similar separation is made by fusion of various mixtures of tin and other metals with sulfur and sodium carbonate followed by extraction with water (Rose's method). Antimony, arsenic, molybdenum, germanium, selenium, and tellurium accompany tin.

The separation of tin from trivalent arsenic and antimony may be accomplished by complexing the tin with oxalic acid²¹ or with hydrofluoric acid²² and precipitating As_2S_3 and Sb_2S_3 . Tin may be separated from cobalt, nickel, copper, and molybdenum by precipitating the tin with ammonia in the presence of a high concentration of ammonium salts.²³ Tin is precipitated by cupferron in 5 to 10 per cent hydrochloric or sulfuric acids by volume.²⁴ Cupferron has been found useful in the separation of tin from aluminum, chromium, manganese, zinc, cobalt, nickel, and alkaline earths.²⁵ Silica is separated from tin by the conventional dehydration procedure, and lead is separated from tin by sulfate precipitation.

Silver, lead, copper, and mercury are separated from tin by electrolytic deposition from a solution containing 5 ml each of nitric and hydrofluoric acids per 100 ml.²⁶ The four elements mentioned together with arsenic(III) and antimony(III) are separated as sulfides from stannic tin in solutions containing hydrofluoric acid (5 ml per 100 ml).^{18, 22, 26}

Arsenic and antimony may be separated from tin by distillation as chlorides; the tin is prevented from distilling by the addition of phosphoric acid.²⁷

2.3 Methods of Determination. If tin has been precipitated as metastannic acid, it may be weighed as stannic oxide after ignition in a porcelain crucible. The oxide that is recovered in this way from bronze and other simple nonferrous alloys is likely to carry oxides of iron, phosphorus, and copper. The weight may be corrected for the oxides of iron, phosphorus, and copper by the sulfur and sodium carbonate fusion method followed by conversion of the residual oxides and sulfides of iron, phosphorus, and copper into a form suitable for weighing. An alternative procedure is to volatilize the tin by heating the ignited oxides with ammonium iodide followed by conversion of iodides of copper, etc., to oxides by nitric acid treatment and heating.²⁸ Stannic cupferrate is converted to stannic oxide upon proper ignition.^{24, 25}

One of the most convenient methods for the macro estimation of tin is the titration of bivalent tin with standard iodine solution. Substances that should be absent are nitric acid, tungsten, molybdenum, and vanadium. Copper, if reduced, does not interfere, but the reduction of quantities greater than 5 mg is uncertain. The tin is reduced to the stannous state by metallic nickel, iron, antimony, or aluminum.^{19, 20}

Few colorimetric methods are available for the estimation of tin. Dithiol (1-methyl-3,4-dimercaptobenzene), which gives a characteristic red color with stannous salts, is very useful.²⁹ An indirect method based upon the reduction of phosphomolybdic acid to molybdenum blue has also been used.³⁰ The range of the methods used is given in Table 12.2.

(a) **Gravimetric Method.** Tin may be determined in uranium tetrafluoride or in other compounds by precipitation of tin as the sulfide, separation by treatment with sodium hydroxide and sodium sulfide solution, and oxidation of the sulfur with peroxide. The acidity is adjusted to 5 per cent sulfuric acid and the solution is cooled. After precipitation with cupferron the tin is finally weighed as stannic oxide.^{31, 32}

Procedure.³¹ A 2- to 3-g sample of UF_4 is weighed into a large platinum dish. An excess of hydrogen peroxide is added, and the sam-

ple is warmed gently until conversion to UO_4 appears to be complete. The liquid is cooled, and 10 ml of HNO_3 and 20 ml of H_2SO_4 (1 to 1) are added. It is then evaporated and heated to fuming; this removes the fluorine. To the cold liquid about 100 ml of water is added, and the sample is heated until solution appears to be complete. Any insoluble matter is filtered off, washed, and ignited at dull-red heat in a silver crucible, and the residue is fused with a little NaOH . The melt is dissolved in the main solution, and the tin is precipitated with

Table 12.2 — Range of Methods

Method	Range
Gravimetric, sulfide-cupferrate	10–50 mg
Colorimetric, dithiol	10–60 γ
Spectrographic, carrier-distillation	1 ppm

H_2S . A little paper pulp is stirred in, the solution is allowed to settle overnight, and then the sulfide precipitate is filtered. The precipitate is treated with a solution of NaOH and Na_2S , filtered, and washed with a Na_2S solution. Hydrogen peroxide is added to the filtrate until it is colorless, and the solution is boiled well to complete the oxidation of polysulfide. The solution is then cooled, dilute H_2SO_4 is added, and the acidity is adjusted to 5 per cent by volume. It is cooled to 10°C , and the tin is precipitated with an excess of an aqueous solution of cupferron that is added slowly with vigorous stirring. A little paper pulp is added to the solution; then it is stirred well and filtered. The precipitate is washed free from sulfate with cold water containing a little cupferron, dried, ignited at red heat, and cooled, and the SnO_2 is weighed.

(b) Colorimetric Method. The dithiol colorimetric method²⁹ has been adapted to the estimation of tin in water samples.³³ The red color that is produced when the reagent is added to dilute stannous solution remains clear for 15 min.

Other metals such as copper, nickel, and bismuth give colors that mask the tin color. These elements are not normally present in water in interfering amounts. They may be removed by extraction at pH 1 to 2 with 0.02 per cent dithizone in chloroform. The useful range is 10 to 60 γ of tin in a final volume of 10 ml. An accuracy of ± 3 per cent may be attained.

Reagents and Standards. The dithiol reagent is melted, and 0.25 ml is dissolved in 10 ml of thioglycolic acid; the mixture is diluted to 200 ml with alcohol.

The tin standards are prepared by dissolving 1.90 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 20 ml of hydrochloric acid, by adding either 20 ml of 10 per cent hydroxylamine hydrochloride solution or 30 g of pure aluminum metal, and by diluting to 1 liter. This solution has a concentration of 1 mg per milliliter and should be prepared fresh each week. Twenty milliliters of stock tin solution and 10 ml of hydrochloric acid are diluted to 200 ml for the preparation of standards.

Procedure.³³ One milliliter of hydrochloric acid is added to a suitable sample of water, usually 200 ml, and the solution is boiled down to less than 10 ml; 0.5 ml of dithiol reagent is added; the volume is adjusted to 10 ml; and the solution is heated in boiling water for 1 min. After cooling, the transmittancy is read at 540 $\text{m}\mu$, and the amount of tin is calculated from a calibration made by running aliquot portions of the tin solution in the same manner. An alternative procedure is to add 1 ml of 0.1 per cent agar-agar solution and to compare the resulting turbidity by reflected light using a series of standards.

3. LEAD

Ores were analyzed gravimetrically for macro amounts of lead, whereas traces in various materials were estimated either by spectrographic, colorimetric, or polarographic methods. The range of methods used is given in Table 12.3.

3.1 Methods of Solution. Nitric acid attack was adequate for uranium and for various alloys. Hydrochloric acid followed by nitric acid attack is in some cases advantageous.¹⁹

3.2 Methods of Separation. Macro amounts of lead are separated by the sulfate method after removal of the acid insoluble group and after separation of the copper and tin groups.^{19,20} Electrolytic separation of lead peroxide effects many separations. The normal interference of bismuth, tin, antimony, and silver may be minimized if a dilute nitric-hydrofluoric acid medium is used.^{19,20}

3.3 Methods of Determination. (a) Gravimetric Method. The gravimetric determination of macro amounts of lead was often required. In ores and minerals the conventional sulfate method was employed.³⁴ It was shown that the isolation as sulfate followed by solution in ammonium acetate, precipitation as sulfide, and eventual conversion to lead molybdate could be applied to uranium.³¹

(b) Polarographic Method. The general scheme for trace analysis that was developed involved deposition of reducible metals in mercury, distillation of the mercury, and solution and polarographic estimation of copper, lead, cadmium, etc. The polarographic estimation of lead agrees fairly well with the colorimetric estimation in the microgram range.^{35,36}

(c) Colorimetric Dithizone Method. A method described by Schultz and Goldberg³⁷ has been found to be simple and reasonably accurate when applied to uranium. The sample is dissolved in nitric acid, complexed with ammonium citrate, and made ammoniacal. The lead with some interfering elements is extracted with a chloroform solution of dithizone. The complex is decomposed with nitric acid, and the lead is reextracted from ammonia-cyanide solution with dithizone. The transmittancy of the chloroform solution containing the lead dithizonate is measured at 510 m μ .

The only other elements, besides lead, that are extracted from alkali cyanide solution are tin(II), thallium(I), and bismuth. Tin and thallium are oxidized during solution and do not interfere. Bismuth, if present, may be extracted at pH 2 with dithizone. Schultz and Goldberg³⁷ found

Table 12.3—Range of Methods

Method	Range
Gravimetric:	
Sulfate	10–200 mg
PbO ₂ electrolytic	10–100 mg
Colorimetric:	
Dithizone	5–20 γ
Polarographic:	
Hg electrolysis-distillation	1 ppm
Spectrographic:	
Carrier-distillation	1 ppm

that aluminum and thallium interfere with the complete extraction of lead by dithizone.

In the range 1 to 20 γ , lead can be determined with an accuracy of 1 γ .

Reagents. Analytical reagent grades of nitric acid, ammonium hydroxide, and chloroform are required. Water is redistilled from a pyrex still and stored in glass-stoppered bottles.

Ammonium citrate, 40 g in 100 ml of water, is purified by making alkaline with ammonia and by extracting with 0.001 per cent dithizone in chloroform until no longer pink. Any dithizone remaining in the aqueous phase is removed by extracting with chloroform.

Sodium cyanide, 10 g in 100 ml of water, is purified in a similar manner with dithizone.

Hydroxylamine hydrochloride, 20 g in 65 ml of water, is treated with an ammonia solution to the *m*-cresol purple end point. Sufficient 4 per cent diethyl dithiocarbamate is added to react with lead and other metals present, and then an excess is added. The solution is

extracted with chloroform until the extract no longer gives a yellow color when it is shaken with copper solution. Final concentration is 20 per cent.

Dithizone, 0.1 per cent stock solution in chloroform, is stored in a refrigerator. A 0.001 per cent solution is prepared when needed and purified by extracting with 1 per cent nitric acid.

Ammonia-cyanide solution is prepared by diluting 75 ml of ammonia solution and 100 ml of 10 per cent purified sodium cyanide to 500 ml.

Procedure. All glassware that is used is washed in nitric acid and rinsed with redistilled water. One gram or less of uranium is dissolved in a slight excess of nitric acid. The solution is transferred to a small separatory funnel, and 3 ml of 40 per cent ammonium citrate is added. Ammonium hydroxide is added to the phenol red point plus 0.5 ml in excess. Next, 0.5 ml of hydroxylamine solution and 1 ml of sodium cyanide solution are added. The solution is then extracted with 5-ml portions of 0.001 per cent dithizone until the last portion is distinctly green. If more than three extractions are necessary, the quantity of reagents used hereafter should be doubled. The extracts are collected in a clean, dry separatory funnel, and the combined portions are shaken 30 sec with 20 ml of 1 per cent nitric acid prepared by diluting nitric acid with redistilled water. The chloroform layer is drawn off and discarded except for 1 or 2 drops. Two drops of *m*-cresol purple indicator are added, and dilute ammonia is added drop by drop to the end point, pH 2. If, upon shaking, a color change is observed in the chloroform, it indicates the presence of bismuth, and it must be removed. This is accomplished by shaking with 0.001 per cent dithizone and discarding the extract. Four milliliters of ammonia-cyanide solution and 2 drops of hydroxylamine hydrochloride solution are added to the aqueous solution, which is then extracted with 10.00 ml of the dithizone solution. The dithizone layer is withdrawn into a cuvette or absorption cell and read spectrophotometrically at 510 m μ against a reference prepared by shaking 20 ml of 1 per cent nitric acid, 4 ml of ammonia-cyanide, and 2 drops of hydroxylamine solution with 10.00 ml of dithizone solution. The concentration of lead is found from a calibration. After the blank has been carried through all steps, the blank reading is subtracted from that of the sample.

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Chapter 13

ALUMINUM, GALLIUM, INDIUM, AND THALLIUM

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This chapter deals with the analytical chemistry of the more common elements of Group III-B.

1. ALUMINUM

1.1 Methods of Determination. (a) Gravimetric Methods. In the analysis of commercial uranium oxide and sodium uranate it has usually been considered sufficient to precipitate aluminum with other insoluble hydroxides, such as those of iron, titanium, and zirconium, by means of ammonium hydroxide and ammonium carbonate and to ignite the combined oxides and report the percentage of "ammonium carbonate insolubles." In all methods employing the ammonium carbonate - ammonium hydroxide separation, some aluminum goes through into the filtrate.

A gravimetric procedure for determining aluminum with ammonium hydroxide after separation of interfering elements was used for uranium-base materials. The aluminum is separated from the ammonium hydroxide group with sodium hydroxide.

(1) Peroxide-Hydroxide Method. This procedure was used in the presence of uranium when the sulfide metals and hydroxide insoluble metals were present. If these ions are known to be absent, the steps provided for their removal may be omitted with the single exception of the sodium hydroxide precipitation. This precipitation must be performed in order to remove the last traces of uranium because the peroxide precipitation is not quantitative.

If only a small amount of aluminum is present, the peroxide precipitation may be replaced by an ammonium carbonate separation; the aluminum is precipitated, and the uranium metal is held in solution as the soluble double carbonate. It is very difficult to filter

large amounts of aluminum and nearly impossible to wash out all the uranium; hence the method described has limited applicability.

Procedure. The uranium-bearing material is dissolved in HCl and HNO_3 . The sample is diluted to volume, and aliquots are taken such that each portion contains about 0.2 g of sample.

The solution is evaporated almost to dryness in order to remove most of the acid. After dilution to 100 ml, the solution is neutralized with NH_4OH , and the acidity is adjusted to 0.2N to 0.3N with HCl. The solution is then heated to boiling, and H_2S is passed through it. It is then cooled, H_2S is passed through again, and the solution is filtered. The precipitate is washed with 1 per cent HCl saturated with H_2S .

To the filtrate is added NH_4OH (1 to 1) until the first permanent precipitate appears, and then 2N HCl is added drop by drop until the precipitate just dissolves. The uranium is precipitated with 30 per cent H_2O_2 using 1 ml per gram of uranium; after this the solution is centrifuged, the liquid is decanted, and the precipitate is washed twice with 0.01N HNO_3 . The washings are added to the decanted liquid, which contains the aluminum.

The solution containing the aluminum is boiled to dryness to remove H_2O_2 , dissolved in warm HCl (5 to 95), and diluted to 100 ml. Five grams of NH_4Cl and 3 drops of methyl red indicator are added, and the solution is heated to boiling. It is then neutralized just to the yellow color of methyl red with 1N NH_4OH , boiled 2 min (adding more NH_4OH if the indicator turns red), and filtered while hot. It is finally washed with 0.5 per cent NH_4Cl wash solution made just basic to methyl red.

The precipitate is dissolved in warm HCl (5 to 95), diluted to 100 ml, and heated to boiling. While the solution is hot, 0.5N NaOH is added until the aluminum hydroxide dissolves. The iron and other insoluble hydroxides are removed by filtering. The filtrate is acidified, and 5 g of NH_4Cl and several drops of methyl red indicator are added. Then 1N NH_4OH is added until the color just changes, and the solution is filtered. The precipitate is washed with NH_4Cl wash solution, and the aluminum is reprecipitated to remove occluded sodium, ignited at 1000°C , and weighed as Al_2O_3 .

(2) 8-Hydroxyquinoline Method. The gravimetric procedure for aluminum in uranium compounds using the 8-hydroxyquinoline precipitation method as given by Lundell and Knowles¹⁶ was used by Haddock¹ for the analysis of uranium oxide.

Procedure.¹ About 2 g of uranium oxide or metal is dissolved in HNO_3 and HCl. The solution is evaporated to dryness, 15 ml of H_2SO_4 (1 to 1) is added, and the solution is evaporated to fumes. The fuming

is repeated to ensure complete removal of HNO_3 . To the cold solution 90 ml of water is added, and the solution is boiled to ensure complete solution. It is then cooled to room temperature and filtered, and the precipitate is washed with cold dilute H_2SO_4 . The filter papers are boiled with 50 ml of ammonium acetate solution (20 g of $\text{CH}_3\text{COONH}_4$ in 100 ml of H_2O) to remove any PbSO_4 . The residue and papers are ignited in a platinum crucible and fused with a little KHSO_4 , and the melt is extracted by warming it with H_2SO_4 . The solution is filtered and combined with the main solution. Then H_2S is passed into the solution for 5 min and digested for 15 min on a hot plate. If molybdenum and/or arsenic are present, the solution is washed into a pressure bottle, and the H_2S solution is heated in a hot-water bath for 1 hr under slight pressure. The precipitated sulfides are filtered and washed with dilute H_2SO_4 (1 to 49) containing H_2S . The solution is boiled down until H_2S is removed, and 0.1N permanganate is added to the hot solution until a permanent pink color is obtained. The volume of the solution is adjusted to 100 ml. The solution is cooled under running water and transferred to a separatory funnel. Five milliliters of a fresh aqueous solution of cupferron containing 0.20 g of cupferron is added drop by drop with vigorous shaking. The cupferrates are extracted with 10-ml portions of chloroform until the latter is colorless. Enough time is allowed between extractions to get a good separation of the two layers; a little of the chloroform should be left in the funnel to avoid loss of aluminum. The cupferron in the aqueous layer is destroyed by evaporation with nitric acid. The solution is neutralized with NH_4OH , HCl is added in slight excess, and then 15 ml of 8-hydroxyquinoline solution is added. A solution of 35 g of $(\text{NH}_4)_2\text{CO}_3$ in 100 ml of water is prepared and cooled, and while stirring vigorously the uranium solution is slowly added to it. The liquid is allowed to stand for 1 hr without further heating, it is filtered through a Whatman No. 40 filter paper, and the precipitate is washed with cold water. The precipitate is rinsed back into the beaker with water, the filter paper is refolded, the beaker is placed under the funnel, hot HCl is poured onto the filter, and finally it is washed a few times with hot water. The solution is heated, if necessary, to dissolve the precipitate completely. The solution is neutralized with NH_4OH , a slight excess of HCl and 5 ml of 8-hydroxyquinoline solution are added, and then the solution is slowly poured into a well-stirred solution of 15 g of $(\text{NH}_4)_2\text{CO}_3$ in 50 ml of cold water. The liquid is allowed to stand and is then filtered as described for the first precipitation. The precipitate is dissolved in HCl as described above. Ammonium hydroxide is added to this solution until the hydroxyquinolate is just precipitated, and the solution is cleared with a slight

excess of HCl; 5 ml of 8-hydroxyquinoline solution is added, the solution is heated to about 50°C, and 100 ml of ammonium acetate solution (20 g of $\text{CH}_3\text{COONH}_4$ in 100 ml of H_2O) is added slowly with stirring. The liquid is allowed to stand for 1 hr without further heating, and the precipitate is collected in a tared sintered-glass crucible (G-4). The precipitate is washed with hot water and dried at 120 to 140°C. The dried precipitate has the composition $\text{Al}(\text{C}_9\text{H}_6\text{OH})_3$ and contains 5.87 per cent Al.

If the sample contains zinc, nickel, or cobalt, the hydroxyquinolates of these metals are precipitated along with the aluminum hydroxyquinolate. In this event they are separated in the following manner: The precipitate is dissolved in hot HCl, and the hydroxyquinoline is decomposed by oxidation with H_2SO_4 and HNO_3 . To the diluted solution is added 0.5 g of tartaric acid followed by NH_4OH in slight excess. H_2S is passed through the solution for 10 min, the liquid is heated to 90°C, and this temperature is maintained for 1 hr.

The sulfides are allowed to settle (if the precipitate is small, it should be allowed to stand overnight). The precipitate is collected on a filter paper and washed with H_2S water. The filtrate is evaporated, and the tartaric acid is destroyed by fuming with HNO_3 and H_2SO_4 . The aluminum is finally precipitated with 8-hydroxyquinoline from the slightly acid solution in the presence of 100 ml of ammonium acetate solution as described above.

(b) Colorimetric Methods. For the determination of aluminum in microgram quantities in uranium compounds several colorimetric procedures have been reported. Hematoxylin and aurin tricarboxylic acid were used for the analysis of uranium-base materials. A solution of 8-hydroxyquinolate in chloroform was employed for beryllium-base materials, and alizarin red S was employed for the analysis of magnesium-base materials.

(1) Hematoxylin Method. Under properly controlled conditions, aluminum gives a bluish-purple lake with the organic dye hematoxylin.^{2,3} For spectrophotometric analysis it is necessary to add a protective colloid to keep the aluminum-hematoxylin lake in suspension. Starch is an efficient protective colloid, and it has the advantage of slightly intensifying the aluminum color, probably by improving the dispersion of the lake. Since the color of the dye is very sensitive to pH, a buffered solution must be used.

Iron gives a slightly less sensitive test with hematoxylin than does aluminum; 1 γ of iron is equivalent to 0.4 γ of aluminum when measured at 610 $\text{m}\mu$. With up to a fivefold excess of iron, aluminum can be determined by applying a correction for the iron concentration found by some other method. An alternate procedure suggested by

Knudson, Meloche, and Juday⁴ is to make use of the difference in the spectral transmittancies of the two lakes as shown in Fig. 13.1 and to calculate the concentrations from the transmittancies measured at two different wavelengths. This method has been used successfully by making measurements at $610\text{ m}\mu$ for aluminum and at $730\text{ m}\mu$ for iron.

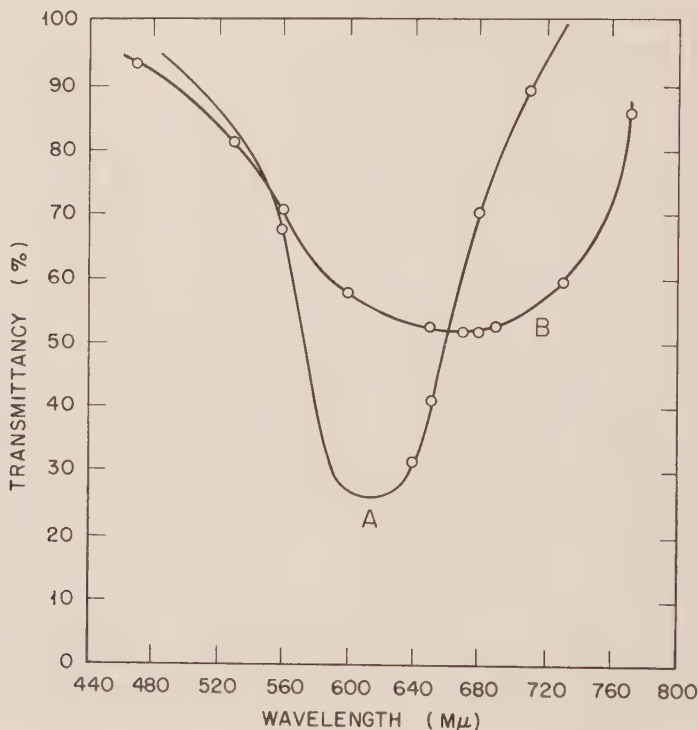


Fig. 13.1—Spectral-transmittancy curves for the aluminum and iron-hematoxylin complexes. Curve A, 10γ of aluminum in 50 ml; curve B, 10γ of iron in 50 ml. Measurements were made with Coleman 10S spectrophotometer, $30\text{ m}\mu$ slit.

In general, moderately high concentrations of arsenic, barium, cadmium, calcium, copper(II), nickel(II), and uranium(VI) do not interfere. Moderately high concentrations of chromium(III), cobalt(II), lead, lanthanum, manganese(II), silver, tin(II), titanium, and vanadium do interfere.

The method may be used for the determination of 0.3 to 10γ of aluminum with an accuracy and precision of about 5 per cent in the absence of interfering elements.

The following method has been employed for the determination of aluminum in uranium-base materials.

Procedure. An aliquot of the sample solution is titrated with ammonium carbonate in order to determine the amount necessary to reach the methyl red end point. A corresponding volume of ammonium carbonate is added to another aliquot, containing up to 10%, in a 50-ml glass-stoppered volumetric flask. The following reagents are added in order: 10 ml of buffer solution (pH = 6; 154 g of $\text{CH}_3\text{COONH}_4$ and 109 g of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ are dissolved in water, 6 ml of glacial CH_3COOH is added, and the solution is diluted to 1 liter), 1 ml of 1 per cent starch solution (1 g of boric acid is dissolved in 95 ml of hot redistilled water, and then 1 g of soluble starch is made into a paste with water, poured into the boiling boric acid solution, and boiled for a few minutes), 1 ml of 0.1 per cent hematoxylin (0.1 g of hematoxylin, Eastman reagent No. 309, is dissolved in 100 ml of boiling water, boiled a few minutes, and filtered), and 20 ml of saturated ammonium carbonate solution. The sides of the flask are washed down, the contents are mixed, and after 12 to 20 min 1 ml of CH_3COOH (3 to 10) is added. After evolution of CO_2 has ceased, the solution is diluted to volume. The transmittancy at 610 $\text{m}\mu$ is measured and compared with a standard curve. If the sample contains iron it is necessary to make a correction for the amount of iron present. This may be done according to the procedure of Knudson et al.^{4,8} by making transmittancy measurements at 610 $\text{m}\mu$ for aluminum and at 730 $\text{m}\mu$ for iron.

(2) Aluminon Method. Aluminum in the ionic form reacts with aluminon (aurin tricarboxylic acid) in buffered solution to form a red lake.

The color may be produced in slightly acid medium,^{5,10} in slightly basic medium,⁶ and in a neutral medium.⁷

Beryllium, chromium, and iron form lakes that interfere, and therefore they must be absent. Ammonium carbonate with ammonium hydroxide is used for neutralizing the acid solution to eliminate the interference of the alkaline earths, the rare earths, zirconium, and gallium, and to complex uranium. Acetone is used to stabilize the lake formed. The procedure given below may be used for the determination of aluminum in uranium-base materials.

Procedure (Alkaline Medium). To an approximately neutral solution 5 ml of HCl and 5 ml of glacial acetic acid are added, and the solution is cooled to room temperature. Five milliliters of 0.2 per cent aurin tricarboxylic acid reagent is added. A filtered mixture consisting of equal amounts of NH_4OH and saturated $(\text{NH}_4)_2\text{CO}_3$ solution is added with stirring until the cloudy appearance of the dye disappears, but the solution is still acid to litmus. A piece of litmus paper

is placed on the side of the beaker, and the $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$ mixture is added, with constant stirring, in the following manner: at the rate of 1 drop every 2 sec until 2 ml is added, then 1 drop every 3 to 4 sec until the litmus is blue. Five milliliters of glacial acetic acid is added, and the solution is left to stand 10 min and then neutralized as above. Finally 5 ml of the $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$ mixture in excess is added. When cooled to room temperature the solutions are compared in 150-ml beakers with standard aluminum solutions treated by exactly the same procedure.

Procedure (Neutral Medium).⁷ To 20 to 25 ml of the sample solution containing 10 to 100 γ of aluminum are added 5 ml of HCl and 5 ml of glacial CH_3COOH . One and one-half grams of $\text{CH}_3\text{COONH}_4$ is added with stirring followed by 20 ml of acetone and 5 ml of 0.2 per cent aluminon solution. (The aluminon solution is prepared by dissolving 2 g of aurin tricarboxylic acid in a minimum quantity of NH_4OH and diluting it to 1 liter with water.) Solid $(\text{NH}_4)_2\text{CO}_3$ is added until the pH of the solution is between 4 and 5. The solution is allowed to stand 15 min to obtain full color development, neutralized with NH_4OH to a pH of 7, and then diluted to 100 ml with a 20 per cent acetone solution. A blank is prepared by the same procedure from an aluminum-free uranium solution containing approximately the same amount of uranium as the unknown. The transmittancy of the sample is determined against the blank at 450 $\text{m}\mu$ with a Beckman spectrophotometer, and the aluminum content is obtained from a calibration curve made with samples of uranium solutions containing known amounts of aluminum.

Procedure (Acid Medium).¹¹ A 2-ml aliquot of an HCl solution is transferred to a 50-ml calibrated test tube and diluted to the 12.5-ml mark with distilled water. The solution is mixed well, and 20 ml of aluminum reagent is added. (The aluminum reagent is prepared by dissolving 154 g of $\text{CH}_3\text{COONH}_4$, 5 ml of HCl, 0.4 g of the ammonium salt of aurin tricarboxylic acid, and 1 g of gum arabic in H_2O and diluting it to 1 liter.) The sides of the tube are rinsed down with 5 ml of water, and the solution is again mixed well. It is then placed in a boiling-water bath for 10 min; after this it is cooled in a water bath at room temperature for 5 min and transferred to a 50-ml volumetric flask. The solution is diluted to volume and mixed well, and the transmittancy is determined with a filter photometer using a green filter (500 to 570 $\text{m}\mu$) against a blank solution identical to the sample solution except that it contains no aluminum. The aluminum is determined by reference to a prepared calibration curve.

(3) 8-Hydroxyquinoline. The colorimetric determination of aluminum by extraction with a chloroform solution of 8-hydroxyquinoline, which was based on the work of Moeller,¹⁷ at pH 4.4 and by spectro-

photometric estimation at $395\text{ m}\mu$ was applied to the analysis of perchloric acid solutions of beryllium metal and oxide. Most interfering elements were removed by mercury cathode electrolysis. It was found that beryllium also reacted with a large excess of oxine to give a product that was also partially extracted at pH 4.4. Some variations of the extraction blank with composition of the sample solution were investigated, and a procedure was developed whereby beryllium containing 0.1 per cent aluminum can be analyzed with a probable error of less than 10 per cent.

Procedure (for Beryllium-base Materials).⁹ To 0.5 g of beryllium, or 1.39 g of beryllium oxide, in a 250-ml Erlenmeyer flask are added 15 ml of water, 2 ml of HNO_3 , and 15 ml of 70 per cent HClO_4 (a few milliliters at a time). After the reaction has subsided, the solution is evaporated to fumes and then fumed at about 200°C for 15 min. (Beryllium oxides are covered and fumed about 30 min longer.) The sample is cooled, dissolved in water, and filtered through a Whatman No. 42 filter paper. Any residue is saved for a separate analysis. The filtrate and washings are diluted to 200 ml and electrolyzed with a mercury cathode, 3 in. in diameter, at about 1.7 amp for 30 min. The electrolyte is separated and diluted to volume. An aliquot containing about 50 mg of beryllium was transferred to a beaker, and a duplicate aliquot was transferred to a separatory funnel. The aliquot in the beaker is diluted with water to about 40 or 45 ml and then adjusted to $\text{pH } 4.4 \pm 0.2$ with filtered CH_3COONa (272 g of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in 300 ml of water filtered through a Whatman No. 40 filter paper). The pH is measured with a glass electrode. The same amount of 4N CH_3COONa is then added to the aliquot in the separatory funnel, and the solution is diluted with a measured amount of water to 50 ml. The solution is extracted by shaking for 30 sec with four 10-ml portions of 0.1M oxine in chloroform (14.4 g of 8-hydroxyquinoline per liter of CHCl_3). The extract is diluted to 0.04M oxine with chloroform, and about 25 ml is filtered through a Whatman No. 12 filter paper to remove water. The transmittancy of the filtered solution is measured against chloroform at $395\text{ m}\mu$ using cylindrical cells 15 mm in diameter and a Coleman 10S spectrophotometer.

An approximate blank correction for the oxine and beryllium effects is made by measuring the transmittancy of a fifth oxine-chloroform extract and by assuming this to be the same as that of a pure (aluminum-free) beryllium solution. The results are obtained from a curve constructed by adding and extracting known amounts of aluminum to a solution purified by the above procedure. The optical density of both test solution and known solutions are corrected for the beryllium oxide blank.

(4) Alizarin Red S. Alizarin red S^{12} was used for the analysis of uranium-base materials at Princeton.¹³ The red salts of calcium, strontium, barium, zinc, and magnesium are readily soluble in cold dilute acetic acid and do not interfere with the coloration due to aluminum.¹² Iron, copper, chromium, cobalt, and manganese interfere. In an extensive investigation by Haywood, Harrison, and Wood¹⁴ effects of concentration, pH, time, and temperature were determined. Spectral-transmittancy curves for the alizarin red S solution and the alizarin-aluminum complex are shown in Fig. 13.2.

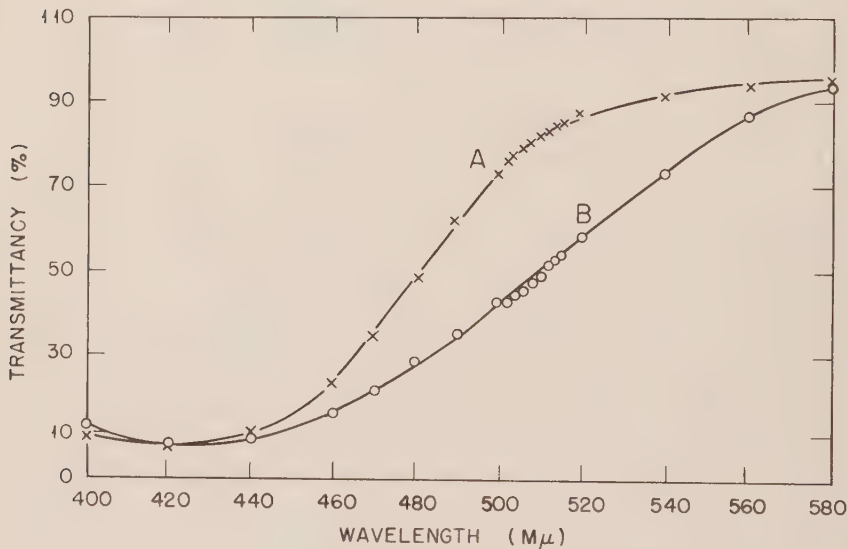


Fig. 13.2—Spectral-transmittancy curves for the alizarin red S and the aluminum complex. Curve A, aluminum-alizarin red S complex; curve B, alizarin red S solution. Measurements were made with a Beckman spectrophotometer.

By electrolysis with a mercury cathode, interfering elements are removed. The method is sensitive to 1 part in 17 million.¹³ The following procedure has been applied to the determination of aluminum in magnesium-base materials.

Procedure.¹³ A 5-g sample of magnesium is dissolved in H_2SO_4 . The aluminum, together with iron, copper, and chromium, is removed by a double precipitation with NH_4OH at a pH of 5.5 to 6.0, and the precipitate is taken up with CH_3COOH (1 to 2). To effect the removal of iron, copper, and chromium from aluminum the solution containing 0.5 ml of excess H_2SO_4 is electrolyzed with a mercury cathode, and

the solution is then evaporated to remove the excess H_2SO_4 . The residue is taken up with CH_3COOH (1 to 2), the solution is diluted to volume, and the proper aliquot is taken for the determination. The aliquot is diluted to about 50 ml with water in a 100-ml beaker, and the pH is adjusted to 4.0. Five milliliters of the dye reagent (2 g of alizarin red S is dissolved in 500 ml of distilled water, and the solution is filtered and diluted to 1,000 ml) is then added, and the solution is transferred to a 100-ml volumetric flask and diluted to the mark. After 15 to 30 min the color is read on a spectrophotometer at a wavelength of $510 \text{ m}\mu$ against the dye solution blank. The transmittancy-concentration curve is made with known amounts of aluminum under the above conditions.

2. GALLIUM, INDIUM, AND THALLIUM

A preliminary report on the colorimetric determination of thallium in uranium compounds is given by Williams.¹⁵ In this method the thallium is separated from the uranium by extraction as the diethyldithiocarbamate, any lead or bismuth present is removed by extraction of their dithizonates in the presence of pyrophosphate, and the thallium remaining in the aqueous solution is determined colorimetrically with dithizone. The method, however, does not appear to be very satisfactory.

Spectrographic methods may be used to determine traces of these elements.

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Chapter 14

ZINC, CADMIUM, AND MERCURY

By N. H. Furman and K. J. Jensen

The estimation of zinc and cadmium, particularly the latter, was frequently necessary in connection with a great variety of materials that were used throughout the Project. The determination of mercury was often called for because of the hazard to health that accompanied its use in various pieces of equipment.

1. ZINC

No novel methods were developed for the macro determination of zinc. In addition to the customary macro methods such as the precipitation of the double phosphate, the ferrocyanide titration, deposition in a mercury cathode, and precipitation as the sulfide, further study was given to the use of organic reagents such as 8-hydroxyquinoline, diethyldithiocarbamate, and 8-hydroxyquinaldine.¹ Electrolytic deposition of zinc was used for zinc-thorium alloys. The chief interest was in the estimation of traces of zinc in uranium or in the raw materials and intermediates that were used in its preparation. The dithizone extraction method^{2,3} was much used as was a combination of electrolysis and polarography.^{4,5} The spectrographic method using the carrier-distillation technique (see Chap. 26, "Spectrochemical Methods") was of considerable value.

1.1 Methods of Solution. Normal samples containing macro amounts of zinc are in general soluble in nitric acid, hydrochloric acid, or a mixture of the two acids. Fusion of the acid-insoluble residue with sodium carbonate may occasionally be necessary. Uranium and its oxides are dissolved in nitric acid, or the metal may be attacked first with hydrochloric acid and then with nitric acid. Uranium tetrafluoride is dissolved by treatment with aluminum chloride and hydrochloric acid.⁶

1.2 Methods of Separation. The well-known separation of the acid-insoluble hydrogen sulfide group is known to cause losses of zinc. The separation of cadmium, cobalt, nickel, copper, antimony, bismuth, and tin from zinc by aluminum after nitric-hydrochloric-sulfuric acid attack and removal of lead sulfate has long been practiced in ore analysis (Waring's method). The zinc is separated as the sulfide in a solution of pH approximately 2 in either a sulfate-sulfuric acid buffer solution or in a formate-formic acid buffer solution.

Extraction with cupferron and chloroform serves to separate iron, vanadium, titanium, molybdenum, zirconium, etc., from zinc.

The extraction of zinc by dithizone and carbon tetrachloride is made much more selective if diethyldithiocarbamate is added.² This method is therefore of considerable utility for the estimation of traces of zinc in various substances.

Electrolysis was much used in separating other metals from zinc, for example, copper and lead. A mercury cathode may be used to separate zinc, cobalt, cadmium, lead, nickel, etc., from uranium.⁵ After electrolysis into a small mercury cathode, the mercury may be removed by distillation, and the traces of the elements that remain may be estimated polarographically.^{5,7,8}

1.3 Methods of Determination. A colorimetric method was used to the greatest extent for zinc determination in uranium and uranium compounds. Electrolytic methods were used for zinc-thorium alloys.⁹

(a) **Electrolytic Method.** In the electrolytic determination of zinc in zinc-thorium alloys,⁹ it was found that the regulation of the pH was important. Unless the pH was 5.5 or above, low results were obtained. If a citrate buffer is used, thorium does not precipitate below pH 10. The deposit of zinc was found to be black and powdery; it rubbed off easily unless a considerable amount of acetone was present.

Apparatus. The apparatus used for electrolysis consists of a platinum-gauze cathode that is plated with copper before electrolysis, a rotating platinum anode to serve as both electrode and stirrer, an ammeter, a rheostat, a switch, and two 6-volt storage batteries. The rheostat is used as a potential divider. The batteries and switch are in series with the full resistance of the rheostat (approximately 100 ohms), but the electrode and ammeter are attached in series to a variable portion of this resistance. The commercial electrolytic analytical apparatus using 110-volt alternating current with a transformer and rectifier was found to be unsuitable because the voltage output was too low to give the desired current with the solutions used.

Procedure.⁹ The sample of the alloy used should contain 0.01 to 0.2 g of zinc. This sample, about 1 g, is treated with HCl (1 to 1) until

the reaction ceases. Then 5 ml of 60 per cent HClO_4 is added, and the mixture is evaporated to perchloric acid fumes. After cooling, the sides and cover are washed down, and the solution is evaporated to fumes again to remove all traces of chloride and nitrate. When cool, solution is diluted to 15 ml, and 5M NaOH is added until a permanent precipitate forms. This precipitate is just dissolved with formic or acetic acid added dropwise. The solution is diluted to 100 ml; 15 g of sodium citrate is added (5 g for each 0.3 g of thorium in solution) and dissolved by warming. The solution should now be slightly alkaline to methyl red. If it is not, just enough 5M NaOH is added to make it so. Fifteen milliliters of acetone is added, and the zinc is electrolyzed onto the cathode, which has been previously copperplated, for 1.5 hr at 1.5 amp. The electrodes are slowly removed from the solution without stopping the current, the cathode being washed with distilled water as it is removed. The cathode is then washed in alcohol and ether and dried at 100°C for 1 min. The zinc is weighed as the metal.

(b) Colorimetric Method. The colorimetric procedure for the determination of zinc using dithizone as developed by Cowling and Miller² has been found applicable to the analysis of small amounts of zinc in uranium metal.^{3,10} Ammonium citrate is used to complex the uranium. All the metals that form dithizone complexes are extracted in carbon tetrachloride at a pH of 8.3 to 8.5 from a solution of the metal sample and ammonium citrate. Zinc, cadmium, lead, and thallium, if present, are extracted into a dilute acid phase. If the extraction is carried out in the presence of diethyldithiocarbamate at a pH of 8.5 to 9.0, the zinc dithizonate is extracted into a carbon tetrachloride layer, but the dithizonates of lead, cadmium, and thallium are not. The diethyldithiocarbamate prevents the formation of the other metal dithizonates much more so than the formation of the zinc dithizonate.² In one method¹¹ the metal dithizonates are extracted with chloroform at a pH of 8.8 to 9.0 in the presence of diethyldithiocarbamate. Zinc is removed from the extract by decomposing its chloroform-soluble diethyldithiocarbamate with sodium hydroxide.

Cowling and Miller² found that the interference of cadmium was greater than that of any of the other metals that form dithizonates, and about half as much cadmium as zinc may be present without causing an appreciable error. Since the cadmium content of uranium was generally below 1 ppm, no trouble was encountered from this interference in analysis of the metal. Care, however, must be taken to minimize contamination errors. All glassware should be carefully cleaned, and the water that is used in the analysis and in the preparation of solutions should be redistilled from an all-pyrex-glass still, unless it is known that the distilled water being used is free from zinc and other

metals that form dithizone complexes. The maximum absorption occurs at 535 $m\mu$. Beer's law is obeyed³ in the range 5 to 100 γ per 100 ml.

(1) Purification of Reagents. Saturated Ammonium Citrate Solution. To the saturated solution is added NH_4OH until it is just blue to thymol blue, and it is then extracted with dithizone solution until the $CHCl_3$ is green. The reagent is washed free from dithizone with $CHCl_3$ and kept in glass free from heavy metals and purified from time to time.

0.2 Per Cent Dithizone. Twenty milligrams of dithizone is dissolved in 100 ml of $CHCl_3$, and the solution is shaken in a separatory funnel with 5 ml of NH_4OH and 50 ml of water. The $CHCl_3$ layer is rejected, the aqueous layer is washed once with 25 ml of $CHCl_3$, and the $CHCl_3$ is again rejected. The aqueous layer is then acidified with HCl , keeping the solution as cool as possible, and extracted with 50 ml of $CHCl_3$; the aqueous layer is rejected. The $CHCl_3$ layer is washed with 100 ml of water, diluted to 100 ml with $CHCl_3$, and stored in an amber glass bottle.

(2) Procedure.¹¹ To about 50 ml of faintly acid aqueous solution in a 100-ml separatory funnel containing not more than about 50 γ of zinc, 5 ml of purified saturated ammonium citrate solution is added, which is followed by a few drops of thymol blue indicator (0.04 per cent in dilute alcohol). The solution is adjusted to a pH of 8.8 to 9.0 by cautiously adding 10 per cent NH_4OH until it becomes just greenish blue; rendering the solution more alkaline than this must be avoided. About 20 mg of sodium diethyldithiocarbamate is added, and the solution is extracted with three successive portions of 10 ml of chloroform. These solvent extracts are mixed in a second 100-ml separatory funnel. The solvent is extracted in the second separatory funnel twice with 20 ml of an aqueous solution containing 4 ml of 20 per cent $NaOH$, 2 ml of saturated ammonium citrate solution, 10 mg of sodium diethyldithiocarbamate, and two drops of concentrated NH_4OH . The solvent layer is rejected.

The combined aqueous extracts from the last operation are acidified with HCl and boiled. A slight excess of bromine water is added, and the excess bromine is boiled off. When colorless the solution is cooled, and 10 per cent NH_4OH is added drop by drop until it is just pink to phenolphthalein (0.05 per cent in 50 per cent alcohol).

The solution is then extracted twice with 5 ml of 0.02 per cent purified dithizone solution diluted with 5 ml of $CHCl_3$. The last solvent extract should be green; otherwise, extraction is incomplete and should be continued. The combined $CHCl_3$ extracts are washed with three

20-ml portions of water containing two drops of NH_4OH . The pink CHCl_3 layer is run into a 10-ml stoppered cylinder, and the volume is adjusted to 10 ml with CHCl_3 . The solvent is centrifuged, and the surface water is removed with filter paper. The transmittancy is measured at 535 $\text{m}\mu$ against a blank that has been carried through the procedure.

2. CADMIUM

The determination of cadmium in various materials has been a matter of considerable importance because of the high value of its cross section for neutron capture.

Interest has centered in distinctive compounds and in methods of separation that might be used in the estimation of traces of cadmium. Certain complex ions containing cadmium are precipitated by organic bases. For example, CdI_4^{--} is precipitated by bases such as brucine and 8-naphthoquinoline. The extraction of cadmium with dithizone and carbon tetrachloride was widely used.

In the preparation of solutions the properties of the material under investigation dictated the method since the solution of cadmium and its compounds presents no problem.

2.1 Methods of Separation. The dithizone extraction method,¹² for which a detailed procedure is given below, was one of the chief methods of separation as applied to uranium and its compounds.¹³⁻¹⁸ This separation was used for concentration of cadmium prior to spectrographic analysis.¹⁹

Small amounts of cadmium were separated from various substances, including uranium and its compounds,^{4,5} by a combination of electrolytic separations. Copper, lead,²⁰ and bismuth²¹ are separated in nitric acid solution by electrolysis onto platinum electrodes. This is followed by electrolysis, whereby cadmium is collected in a mercury cathode. For all substances that contain minor amounts of cadmium, copper, cobalt, iron, nickel, lead, or zinc, a direct electrolysis into a small mercury cathode from weakly acid solution serves to collect the metals. After distillation of the mercury at 360°C, the residue is weighed, dissolved, and examined polarographically.^{7,8}

2.2 Methods of Determination. Macro amounts of cadmium are separated as the sulfide and weighed as the sulfate or the pyrophosphate as described in standard texts.^{22,23} Electrolysis may be used provided interfering elements have been removed.²² Polarographic methods were employed after separating into a mercury cathode as described in Sec. 2.1. This method was applied to thousands of samples of intermediates, accessory materials, and uranium. The method

serves as an independent check on other methods, notably the spectrographic. The procedure appears to be superior to dithizone methods for examination of materials that contain zinc in high ratio to cadmium as is normally the case in magnesium.³⁵

The carrier-distillation method of spectrographic analysis of Scribner and Mullin is described in detail in Chap. 26, "Spectrochemical Methods." This method was the one most frequently applied for the determination of cadmium.

Colorimetric Method. Dithizone has been found especially useful for the determination of small amounts of cadmium in various Project materials (see references 14 to 18 and 24 to 26). The procedures of Fischer and Leopoldi²⁷ and of Sandell²⁸ have been modified so that the method is applicable for the determination of cadmium in uranium. In this procedure all the metals that form dithizone complexes are extracted as their respective dithizonates at a pH of 8.3 to 9.0 in carbon tetrachloride. Citrate is employed to keep the uranium in solution. The organic layer containing all the metal dithizonates is then shaken with 0.01N hydrochloric acid, under which circumstances the dithizonates of cadmium, zinc, lead, and thallium, if present, are decomposed and thus extracted into the aqueous layer. Traces of copper and nickel are also extracted into the aqueous phase. These traces of copper and nickel are removed by extracting the 0.01N acid solution with dithizone in carbon tetrachloride. The aqueous solution is then made basic with sodium hydroxide, ammonium citrate is added, and the solution is extracted with a dilute dithizone-carbon tetrachloride solution. Only the cadmium dithizonate is extracted into the organic layer from the above-mentioned solution. The transmittancy of the extracted cadmium dithizonate is then measured at 520 m μ .

The procedure described below is applicable in the presence of milligram amounts of all the other metals that form dithizonates.²⁴ Zinc cannot be present in amounts much greater than 3 mg. Bricker and Furman³⁵ found that there is a limiting amount of dithizone that may be used when a given amount of zinc is present, for example, 1 mg in 35 ml; the use of 10 ml of 0.002 per cent dithizone is all that is permissible. If extraction is repeated with an additional portion of dithizone, zinc dithizonate is extracted. Traces of copper and nickel are extracted somewhat into the aqueous phase along with the cadmium, zinc, and lead, but these traces are removed by extracting the acid aqueous phase with the dithizone-carbon tetrachloride solution. As in the colorimetric zinc determination, care must be taken to minimize contamination errors.

The range of the method is 1 to 7 γ of cadmium when the dithizonate is extracted in a 10-ml volume of the dithizone-carbon tetrachloride solution. The results are accurate to ± 10 per cent.

The reagents can be purified by the use of dithizone as described in Sec. 1.3b.

Procedure.^{15,24} A 3-g sample of uranium metal, after having been rinsed with ether and distilled water and dried, is dissolved in 3 to 4 ml of HCl followed by 2 to 3 ml of HNO₃. The solution is evaporated to a sirupy state and diluted with 80 ml of water. Ten milliliters of 50 per cent ammonium citrate solution is added, and the solution is washed into a separatory funnel. Two drops of thymol blue indicator solution (0.1 g of thymol blue is dissolved with 2 ml of 0.1N NaOH and 5 ml of 90 per cent alcohol and then diluted to 250 ml with 20 per cent alcohol) are added; this is followed by addition of NH₄OH until the indicator changes from yellow to green. (No more than a few drops of the indicator are added since larger amounts tend to cause low cadmium values.) Five milliliters of NH₄OH is then added in excess. Five milliliters of 0.02 per cent dithizone solution in CCl₄ is added, and the mixture is shaken for 1 min. The phases are allowed to separate, and the CCl₄ layer is drawn into another separatory funnel, using a few milliliters of CCl₄ to rinse down the funnel stem. This extraction procedure is repeated until the extract is green. The combined extracts are then washed with 5- to 10-ml portions of water until the aqueous phase is colorless. The water layers are drawn off with a pipet or other suction device. Ten milliliters of 0.01N HCl is added, and the solution is shaken vigorously for 2 min. After the phases have separated, the carbon tetrachloride layer is discarded. Then 5 ml of 0.002 per cent dithizone solution in CCl₄ is added, the solution is shaken for 1 min, and the phases are allowed to separate. The organic layer is discarded, and the extraction is repeated until the extracts are green in color. Then the aqueous phase is washed with CCl₄ until the extracts are colorless. Five milliliters of 10 per cent ammonium citrate solution and 5 ml of 20 per cent NaOH solution are added to the acid aqueous phase. Ten milliliters of the 0.002 per cent dithizone solution is added, and the solution is shaken vigorously for 2 min. After the phases have separated, a little of the carbon tetrachloride phase is allowed to run out, thus rinsing the stem of the separatory funnel. The rest of the organic layer is transferred to a clean, dry cuvette, and the transmittancy of the solution is measured at 520 m μ against a blank taken through the entire procedure. The amount of cadmium in the sample is obtained from a transmittancy-concentration curve prepared previously. The range is from 10 to 60 γ of cadmium per 100 ml.¹⁵

3. MERCURY

Determinations of mercury were mainly of interest in connection with health hazards. The chief interest in Project work was in the determination of traces of mercury.

3.1 Methods of Determination. (a) Colorimetric Method with Dithizone. The dithizone method has been applied to the determination of mercury in uranyl solutions in various laboratories.^{29,30} This method, which is somewhat modified from the work of Laug and Nelson,³¹ depends upon the fact that mercury is extracted as the salmon-colored complex with dithizone and chloroform.

Dithizone also reacts with palladium, gold, silver, copper, and bismuth at a pH of less than 3. In their work, Delaney, Goldsmith, and Krause³⁰ did not consider the interference of palladium and gold since these elements are so rarely encountered. Small amounts of silver in the presence of 0.25N HCl would not be expected to interfere. The remaining possible interferences, copper and bismuth, were tested in the procedure, and it was found that they could be tolerated in amounts as large as 40 γ of copper and 800 γ of bismuth. Uranium, aluminum, and iron could also be tolerated.

For samples containing large amounts of copper the original Laug and Nelson procedure³¹ or the British method²⁹ would be preferable to the procedure described below.

The method is accurate to within 10 per cent of the true values in the range of 1 to 10 γ of mercury when 10-ml volumes of dithizone solution are used to extract the mercury.

(1) Purification of Reagents. Dithizone Solution. Dithizone, 5.5 mg, purified as for the zinc determination is made up to 1 liter with chloroform.

Ethyl Alcohol. Absolute ethyl alcohol is redistilled over potassium hydroxide from an all-glass still and stored in a pyrex bottle.

Chloroform. One liter of reagent-grade chloroform is shaken with 100 ml of a 5 per cent $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution that has been neutralized with ammonium hydroxide to the phenol red end point. The chloroform is then redistilled from an all-glass still. Redistilled ethyl alcohol is then added to the extent of 1 per cent as a preservative. The purified chloroform is stored in the dark in a tightly stoppered bottle.

0.25N Hydrochloric Acid. Hydrochloric acid (1 to 1) is distilled from an all-glass still into a pyrex container. The normality of the distillate is determined, and the solution is diluted to 0.25N with re-distilled water.

20 Per Cent Hydroxylamine Hydrochloride Solution. Twenty-five grams of reagent-grade $\text{NH}_2\text{OH} \cdot \text{HCl}$ is dissolved in 100 ml of redistilled water. This solution is purified by shaking with two 25-ml portions of dithizone solution containing 100 mg of dithizone per liter.

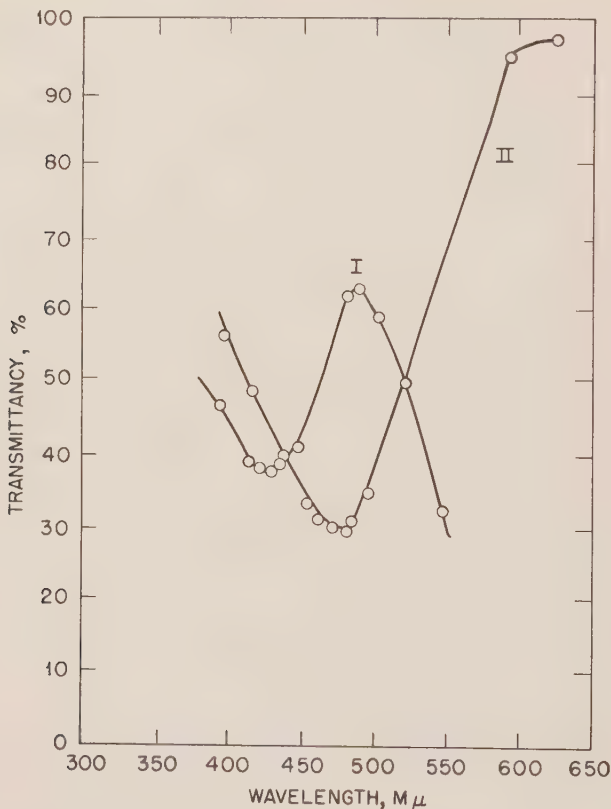


Fig. 14.1—Spectral transmittancy curve.³⁰ I, Dithizone (0.0005 per cent) in chloroform. II, Mercury dithizone complex in chloroform (about 1 γ per milliliter). Measurements were made against chloroform using a Coleman model 10S spectrophotometer; 1.6-cm cylindrical cells.

Traces of dithizone are removed from the hydroxylamine hydrochloride solution by shaking with portions of clear chloroform.

(2) Procedure.³⁰ Fifty milliliters of the 0.25N HCl is placed in a 125-ml Squibb separatory funnel. To this acid solution is added an aliquot of the test solution containing from 1 to 10 γ of mercury. Then

5 ml of the 20 per cent $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 10 ml of the dithizone solution are introduced, and the contents are shaken for 1 min. The layers are allowed to separate, the chloroform layer is transferred to a clean, dry cuvette, and the transmittancy is measured at $490 \text{ m}\mu$ against a blank carried through the entire procedure (see Fig. 14.1). The weight

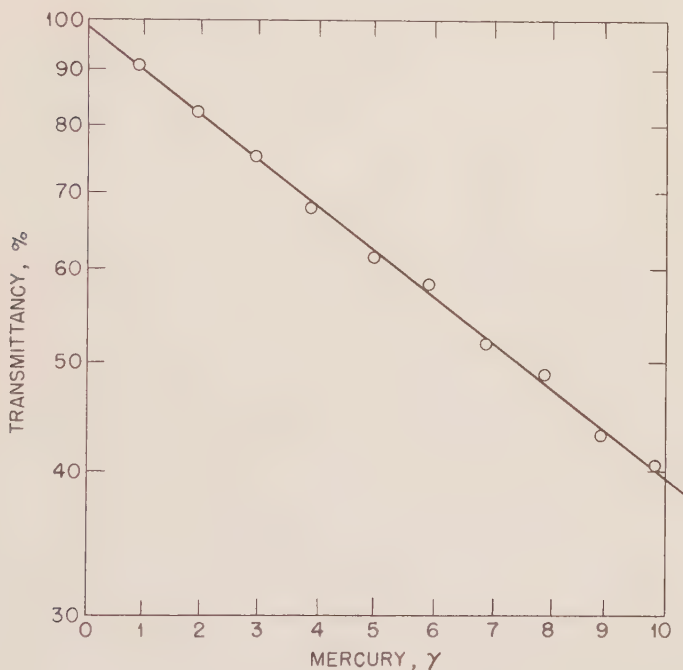


Fig. 14.2—Transmittancy-concentration curve for mercury.³⁰ Solution was prepared as described in text. Measurements were made at $490 \text{ m}\mu$ against a blank carried through procedure, using a Coleman model 10S spectrophotometer; 1.6-cm cells.

of mercury in the aliquot taken for analysis is obtained from a previously prepared transmittancy-concentration curve (see Fig. 14.2).

(b) Turbidimetric Method. The determination of mercury vapor in air is best made by measuring the absorption of radiation at a wavelength of $253.7 \text{ m}\mu$.³² Chemical methods are less satisfactory.

The following method, adapted from work of Palejaev,³³ was used at one installation³⁴ for testing for mercury in air. It is based upon the formation of increasingly intense colored precipitates when mercury iodide is precipitated upon a white cuprous iodide matrix.

Procedure.³⁴ A 30-ml midget impinger flask* is charged with 10 ml of 0.04 per cent iodine solution (0.5 g of iodine and 6 g of KI in 1 liter of H₂O). One cubic foot of the air to be sampled is drawn through the solution at the rate of 0.1 cu ft per minute. A 5.0-ml aliquot from the collection flask is transferred to a test tube, and 1.0 ml

Table 14.1 — Mercury Comparison Standards

Test tube No.	Dilute Hg standard, ml	Distilled water, ml	Equivalent mg of Hg per cubic meter (5-ml aliquot used)
1	0.00	1.00	0.00
2	0.10	0.90	0.05
3	0.20	0.80	0.10
4	0.40	0.60	0.20
5	0.60	0.40	0.30
6	0.80	0.20	0.40
7	1.00	0.00	0.50

of water is added, followed by 0.4 ml of 1M Na₂SO₃ solution. (If an aliquot of less than 5.0 ml is used, the volume should be brought up to 5.0 ml with 0.05 per cent iodine solution.) The tube is mixed by shaking vigorously. To this solution 0.2 ml of CuSO₄ solution is added (15.6 g of CuSO₄·5H₂O diluted to 100 ml with H₂O), and the tube is shaken until the last trace of green color has disappeared. The suspension is compared with standards prepared at the same time, and the results are presented in Table 14.1. The dilute standard solution is prepared by taking 1 ml of a stock mercury solution (0.0963 g of HgCl₂ in 1 liter of H₂O) and diluting to 10 ml with water. To each of the above standards is added 5.0 ml of 0.05 per cent iodine solution. The standards are treated as the unknown starting with the addition of sodium sulfite. The standard tubes are graduated so that, when 1 cu ft of air is sampled and a 5.0-ml aliquot of the iodine is used, the milligrams of mercury per cubic meter is read directly from the standard tube matched.

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Chapter 15

COPPER, SILVER, AND GOLD

By T. D. Price and R. E. Telford

1. COPPER

Copper is frequently determined in uranium and thorium ores, solutions, and refined products. Macro analytical methods are usually suitable for the analysis of ores and solutions, but refined products such as uranium tetrafluoride and uranium metal usually require micro or spectrochemical methods.

Since the analytical chemistry of copper has been well summarized in standard reference books,¹⁻⁵ the present treatment is designed to cover only analytical improvements and new applications of copper analysis as developed on the Manhattan Project.

1.1 Methods of Separation. The classic acid sulfide precipitation of copper has been used primarily for the purpose of separating copper in the course of a rare-earth analysis. However, it is a well-known fact that copper can be quantitatively separated by this method from all cations not in the acid hydrogen sulfide group. The addition of oxalic or hydrofluoric acid to the sulfide solution prevents the precipitation of any tin or germanium with the copper. A sodium sulfide-sodium hydroxide precipitation following the acid sulfide precipitation may be used to separate copper from molybdenum.⁶

Certain organic reagents such as α -nitroso- β -naphthol, α -benzoin-oxime, and salicylaldoxime have been used⁶ to precipitate copper. Palladium and gold are the only interferences in the precipitation of copper with salicylaldoxime.⁵ A method using this reagent is reported for the determination of copper in uranium tetrafluoride.⁷ Gravimetric and turbidimetric variations are described.

Copper in the form of its dithizone complex can be separated from many other elements by chloroform and carbon tetrachloride extractions by using appropriate variations of the acidity, complex-ion con-

tent, etc., of the aqueous solution. It has been shown that copper (also vanadium and iron) can be quantitatively separated from nickel, zinc, and manganese by chloroform extractions of cupric cupferrate at a pH of 0.7 to 0.8 in nitric acid.⁸ Ammonium sulfate was added to ensure complete extraction. This separation was followed by application of the dithizone extraction and a photometric copper determination.

Deposition in a mercury cathode has been found useful for separating small amounts of copper preliminary to polarographic determination.⁹⁻¹⁴

1.2 Determinations. Gravimetric methods for the analysis of copper have not been widely used, but standard procedures involving electrolytic deposition have been employed. Bricker⁷ has suggested the salicylaldoxime precipitation method for the determination of copper in uranium tetrafluoride. Wilder¹⁵ used the α -benzoinoxime precipitation in an ammoniacal citrate solution as a qualitative copper test in the presence of uranium, nickel, chromium, manganese, and iron.

Larson and Price have developed a modification of the iodometric method³ which accomplishes the removal of uranium and nitrite interference and complexes the iron.^{16,19}

Although a large number of reagents may react to give colored substances with copper and are therefore useful for its colorimetric determination, the two most satisfactory reagents are diphenyldithiocarbazon (dithizone) and sodium diethyldithiocarbamate. The dithizone method is more sensitive, and it has the additional advantage that the extraction may be carried out in acid solution. At a pH of less than 3 the dithizonates of gold, platinum, palladium, silver, mercury, bismuth, bivalent tin, and copper are extracted into the chloroform layer. The dithizonates of silver, gold, mercury, bismuth, and tin may be destroyed by shaking the extract with 2 per cent potassium iodide in 0.01N hydrochloric acid. Large amounts of iron interfere.

Sodium diethyldithiocarbamate gives a golden-yellow compound with copper in alkaline solution. This compound may be extracted with isoamyl alcohol, isoamyl acetate, or carbon tetrachloride. Several other elements form colored precipitates that interfere, but steps may be taken to prevent these interferences. Manganese and uranium do not react when complexed with citric acid. Sodium pyrophosphate prevents iron interference. Nickel and cobalt interference are prevented by adding dimethylglyoxime before making the solution alkaline and centrifuging off the nickel precipitate. Bismuth must also be removed.⁷

Several reports^{17,18} describe a procedure for precipitating the copper with H_2S from weak sulfuric acid solutions containing uranium.

The sulfide precipitate is separated and dissolved with hot dilute nitric acid, and copper is determined colorimetrically as the copper-ammonia complex.

(a) Salicylaldoxime Method for Copper in Uranium Tetrafluoride.⁷
Procedure. One gram of sample is decomposed by igniting with 2 g of boric acid in a platinum crucible. The residue is treated with 15 ml of 6N nitric acid and taken to dryness with 0.5 ml of sulfuric acid. After dilution 2N sodium hydroxide solution is added until a permanent precipitate forms; then acetic acid is added until the precipitate dissolves. The copper is then precipitated with 1 ml of 1 per cent salicylaldoxime (1 g of reagent in 5 ml of alcohol diluted to 100 ml

Table 15.1—Methods for Determination of Copper

Method	Reagent or technique	Range	Accuracy
Gravimetric	Electrolytic deposition	0.01–5 g	±0.2 mg
Volumetric	Iodometric titration	0–0.2 g	±0.2 %
Colorimetric	Dithizone	1–5 γ	
		5-ml volume	
	Sodium diethyldithiocarbamate	1–40	±5%
		5-ml volume	
Spectrographic	Carrier distillation	Limit 0.3 ppm	
Polarographic	Electrolysis distillation	Limit 5 γ	

with water). If the copper content is small, that is, between 10 and 100 γ , the sample should be estimated turbidimetrically. If the amount of copper is larger, the precipitate is filtered on a tared sintered-glass crucible, washed, and dried for 1 hr at 105°C; then the crucible is reweighed.

(b) Volumetric Method. (1) Iodometric Method for Copper in Solutions and Solids.^{16,19} This modification of the standard iodometric method³ has been used primarily where a complete analysis of solution of solid samples is desired. Copper, preferably in 20- to 40-mg amounts, can be determined in such products as steel, uranium halides, and various solutions with an accuracy of ±0.2 per cent.

Procedure. The sample, if solid, is dissolved in water, nitric acid, or a hydrochloric acid–hydrogen peroxide mixture. A 5-ml quantity of 4 per cent urea solution is added, and the solution is boiled for 2 min. Dilute ammonium hydroxide solution is added until the first permanent appearance of a precipitate, which is dissolved by the addition of 5 ml of glacial acetic acid. A 10-ml sample of 20 per cent

ammonium bifluoride is then added. (If the iron and uranium content of the sample is thought to be greater than 1.1 g, more bifluoride should be added until a negative spot test for iron is obtained with thiocyanate.) Five grams of potassium iodide is added, and the sample is allowed to stand for 2 min with occasional stirring and is then

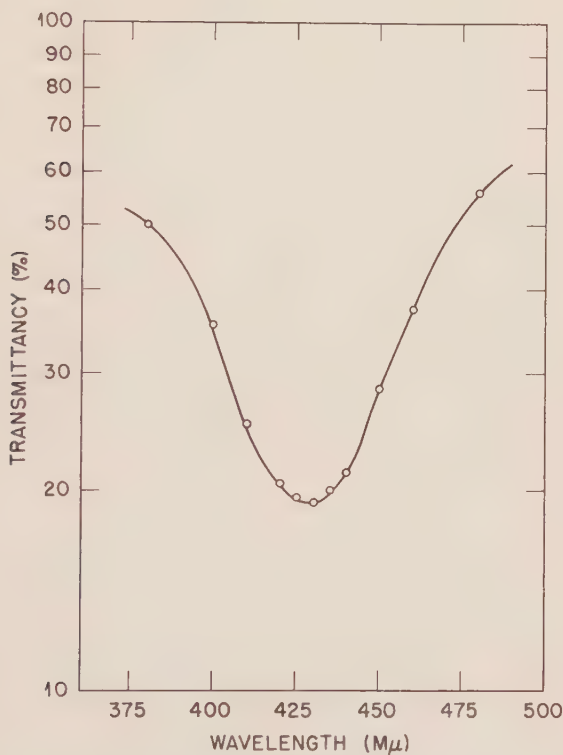


Fig. 15.1—Spectral transmission curve of copper diethyldithiocarbamate in isoamyl alcohol (100 γ of copper per 25 ml), measured in a 1.00-cm cell with a Beckman spectrophotometer against isoamyl alcohol as reference.

titrated rapidly with 0.02N sodium thiocyanate. When the solution is within 1 ml of the end point, 5 ml of 40 per cent ammonium thiocyanate and 2 ml of 1 per cent starch solution are added. If insufficient fluoride has been added, a red ferric thiocyanate color will momentarily result when the thiocyanate is added, and a rerun will be necessary.

(c) Colorimetric Methods. (1) Colorimetric Determination of Copper with Sodium Diethyldithiocarbamate. Sodium diethyldithiocarbamate has been used for the determination of small amounts of copper.²⁰⁻²⁴ When a solution of sodium diethyldithiocarbamate is added to a solution containing small amounts of copper, the golden-yellow

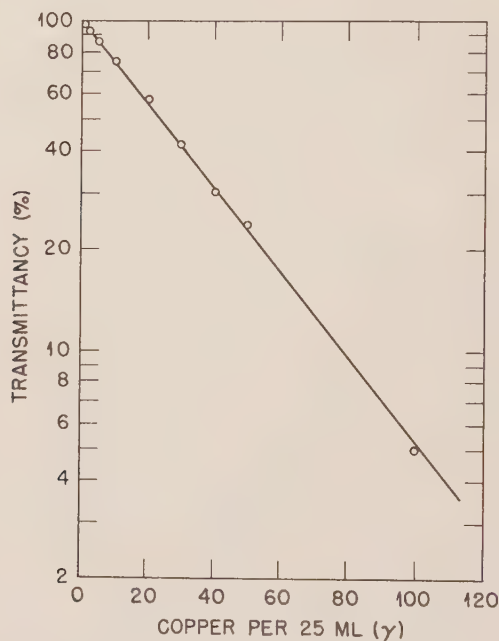


Fig. 15.2—Standard curve for determination of copper as diethyldithiocarbamate in isoamyl alcohol, measured at 430 $m\mu$ with a Coleman model 10S spectrophotometer.

compound formed can be extracted with isoamyl alcohol and the transmittancy measured spectrophotometrically²⁶ (see Fig. 15.1). The copper concentration is found from a standard curve (see Fig. 15.2).

Iron, nickel, cobalt, bismuth, and uranium react with sodium diethyldithiocarbamate to give colored salts that are soluble in isoamyl alcohol. Uranium is complexed with citric acid, and iron(III) is complexed with sodium pyrophosphate, to prevent interference by these elements. Nickel, if present, may be separated by adding dimethylglyoxime and filtering. Dimethylglyoxime also prevents cobalt interference. Bismuth may be separated from the solution by precipitation with excess ammonia.

The accuracy of this method is about 5 per cent, and a precision of 2 per cent may be attained. The useful range is 2 to 50 γ of copper.

Procedure.²⁰ An acidic aliquot containing 2 to 50 γ of copper is transferred to a 25-ml glass-stoppered graduated cylinder. Concentrated ammonium hydroxide is added until the appearance of a precipitate; then 4 ml of 50 per cent nitric acid is added, followed by ammonium hydroxide to pH 9. In order to complex iron 5 ml of 5 per cent sodium pyrophosphate is added. One milliliter of 2 per cent aqueous sodium diethyldithiocarbamate (freshly prepared every few days) is added, and the solution is extracted with 5 ml of isoamyl alcohol. The solution is extracted with two more 5-ml portions of isoamyl alcohol, each portion being removed with a pipet and transferred to a 25-ml volumetric flask. The combined extracts are made up to volume, thoroughly mixed, and filtered if necessary. The transmittancy is then measured at 430 $m\mu$ against a blank of the reagents. The concentration is found from a standard concentration-transmittancy curve prepared by carrying known amounts of copper through the entire procedure (see Fig. 15.2).¹³

(2) Colorimetric Determination of Copper with Dithizone.²⁶ Transmittancy measurements at 540 $m\mu$ may be used for less than 20 γ of copper. Ten times as much nickel, cobalt, zinc, or molybdate as copper does not interfere. Chromate interferes, but it can be reduced to chromic ion by the addition of ethanol during the fuming operation. Chromium(III) does not interfere when present in tenfold excess over the copper.

Procedure. A sulfate solution is prepared from 1 g of UF_4 samples, or 1 g of the metal, by fuming off excess sulfuric acid. For each 10 ml of the solution 2 ml of 10 per cent sulfuric acid should be added. Dithizone (4 mg per 100 ml of CCl_4) is added in 1- to 2-ml portions; then the mixture is shaken in a separatory funnel, and the carbon tetrachloride layer is drawn off. The extraction is continued with fresh 1- to 2-ml portions of dithizone solution until a pure green extract is obtained, whereupon the aqueous layer is washed with 2 ml of pure carbon tetrachloride. The combined extracts are washed with 10 ml of NH_4OH (1 to 200). The carbon tetrachloride layer is then drained into a 25-ml volumetric flask. The ammonia layer is washed with 3 to 5 ml of carbon tetrachloride. The combined carbon tetrachloride layers are diluted to 25.00 ml with additional carbon tetrachloride, and the transmittancy of the solution is read at 540 $m\mu$. The color is fairly stable, but the transmittancies should be read within 30 min. A calibration curve is prepared in a similar manner.

(d) Polarographic Method. The polarographic method for analysis of microgram quantities of copper³¹ has been used.^{12,13} Copper was determined in pyridine-buffered (pH 5.15) and ammoniacal solutions after electrolysis into mercury, distillation of the mercury, and solu-

tion of the residual metal in hydrochloric acid. Polorographic procedures are described in detail in Chap. 25 on "Electrometric Methods."

(e) Spectrographic Method. The carrier-distillation technique of spectrographic analysis can be used for the determination of traces of copper (see Chap. 26 on "Spectrochemical Methods").

Table 15.2—Methods for Determination of Silver

Method	Reagent	Range
Colorimetric	Dithizone	1–15 γ
		5 ml solution
	<i>p</i> -Dimethylaminobenzilidene-rhodanine	1–40 γ
Spectrographic		25 ml solution
	Carrier distillation	Limit 0.05 ppm

2. SILVER

Analytical development work has been done mostly on spectrographic methods for silver. The spectrochemical procedures for silver analysis are given in Chap. 26 on "Spectrochemical Methods."

One report²⁵ describes a successful application of the dithizone separation, followed by the spectrographic determination of silver. The details of this procedure are summarized as follows: The aqueous sample containing 0.5 to 10 γ of silver (also uranium and other elements) is diluted to 15 ml. A 2-ml sample of dilute nitric acid is then added, and the mixture is extracted with 5-ml portions of 0.01 per cent dithizone solution (in carbon tetrachloride) until the organic layer is no longer red on separation. The solvent extracts are then combined, washed with a few milliliters of very weak nitric acid, and filtered through a small cotton plug. The combined extract is now evaporated to a small volume, further taken to dryness on a copper electrode, treated with a few drops of HCl, reevaporated, cautiously flamed with a bunsen burner, and examined spectrographically for silver.

It was demonstrated that care must be taken to avoid long contact between silver solutions and glassware because of adsorption of silver on the latter. The loss of silver by combination with platinum at high temperatures was also demonstrated in this report.

3. GOLD

Ores and refined products have been analyzed for gold. Ores are analyzed because of the value of gold as a by-product, and some re-

fined products are checked for traces of gold. The final determination is usually made spectrographically.

3.1 Methods of Separation. Many separation methods have been described in the analytical literature.^{3,5,26} Traces of gold are usually separated by means of a dithizone extraction or by a precipitation

Table 15.3—Methods for Determination of Gold

Method	Reagent	Range
Colorimetric	Reduction by SnCl_2	10–100 γ
		25-ml volume
	<i>p</i> -Dimethylaminobenzilidene-rhodanine	1–25 γ
Spectrographic	Carrier distillation	25-ml volume
	Copper spark	Limit 0.3 ppm Limit 0.02 γ

utilizing metallic tellurium as a carrier for metallic gold. Procedures for these separations are described below.

3.2 Methods of Determination. Gold may be determined either by direct spectrographic examination of solid or liquid samples or by partial purification and a final spectrographic determination. Two other procedures are also briefly presented.

(a) Analysis of Gold in Ores and Other Materials.²⁷ In this procedure the uranium is removed by hydroxide precipitation, and the gold and platinum are coprecipitated with tellurium. They are then determined spectrographically.

Procedure.²⁷ To a 1-g sample are added 350 ml of H_2O and 10 ml of HCl (1 to 19). The sample is heated to boiling, 10 ml of 10 per cent NaBrO_3 is added, and digestion on a steam bath is continued for 1 hr.

After digestion the sample is again heated to boiling, an additional 5 ml of bromate solution is added, and the sample is cooled. Then 10 per cent NaOH is slowly added until a pH of 10 is obtained. The solution is next brought to a boil to coagulate the uranium precipitate. The precipitate is filtered off on a Whatman No. 42 filter paper and discarded.

Twenty milliliters of HCl (1 to 19) is added to the filtrate, which is then evaporated to dryness on the steam bath. The dry residue is dissolved in 2N HCl and again evaporated to dryness. These dissolving and evaporating steps are then repeated. The final residue is dissolved in 30 ml of hot 2N HCl until the filtrate is approximately 50 ml. Ten milliliters of the tellurium solution [10 mg of tellurium per milliliter is prepared as follows: Five grams of tellurium powder

is dissolved in 15 ml of HCl (1 to 19) and 5 ml of HNO_3 and evaporated to dryness. The solid is dissolved in HCl (1 to 19) and again evaporated to dryness. This operation is repeated. The final residue is dissolved in 2N HCl and filtered through a Whatman No. 42 filter paper, which is well washed with water, and the filtrate is diluted to 500 ml with 2N HCl] is added to the sample, and the gold and tellurium are coprecipitated by adding slowly, with constant stirring, 10 ml of 20 per cent SnCl_2 solution (20 g of SnCl_2 is dissolved in 17 ml of HCl and diluted to 100 ml). The precipitate is coagulated by heating and stirring and is then allowed to stand overnight.

The supernatant solution is tested for completeness of precipitation by the addition of a little more SnCl_2 solution. If the test is negative, the precipitate is filtered, using a 30-ml tared sintered-glass crucible of fine porosity. The precipitate is washed several times with cold 2N HCl, once with alcohol, and finally with ether. The precipitate is then dried for 1 hr at 100°C , cooled, and weighed.

A 15-mg portion of the dry precipitate, the total of which should weigh between 90 and 100 mg, is mixed with 5 mg of graphite and completely burned on a graphite electrode by using a d-c arc. The gold lines are compared either with the lines from a set of standards containing known amounts of gold or with a tellurium line as internal standard. The 2675.95 and 2748.26 Å gold lines and the 2967.2 Å tellurium line are used.

(b) Miscellaneous Methods. One report²⁵ on the analysis of gold, designed for trace constituents, involves carbon tetrachloride (or chloroform) extraction of the gold dithizonate from an acid medium, evaporation of the extract to dryness on a copper electrode, and spectrographic evaluation of the gold content. The procedure is the same as the one given for silver, except that the spectrogram is compared with a set of gold standards using the 2675.95 Å gold line.

A second procedure²⁸ consists in a volumetric method designed for the analysis of gold in uranium-alloy samples.

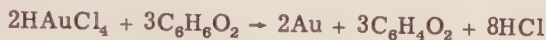
In this procedure the alloy is readily attacked by nitric acid (sp.gr. 1.2). It yields a solution containing only a very small amount of gold (<0.05 mg), together with a residue containing nearly all the gold and some tin and uranium. The soluble portion of gold can be recovered by carrying it with tellurium in a hydrochloric acid solution as described above, but it is generally regarded as a negligible constituent.

The determination of gold in the insoluble residue is made in general accordance with the earlier work of Pollard²⁹ and Jamieson and Watson.³⁰

The residue is dissolved in bromine water, to which has been added a little concentrated hydrochloric acid; the excess bromine is re-

moved by aeration; and the resulting solution is treated with potassium acid fluoride buffer reagent.

The solution is then titrated with standard hydroquinone solution by using *o*-tolidine (or *o*-dianisidine), which is added toward the end of the titration as the indicator. The end point is the disappearance of the intense yellow color formed by the oxidation of the indicator with chlorauric acid. The hydroquinone reduction of chlorauric acid proceeds according to the following equation:



Tests showed that small amounts of uranium do not interfere with this reaction.

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Chapter 16

IRON, COBALT, AND NICKEL

By R. W. Bane and W. R. Grimes

1. IRON

Iron was found to be present in a great many of the raw materials used on the Project. Methods for the determination of iron and for the separation of iron from uranium have, accordingly, been studied.

1.1 Methods of Solution. Uranium metal or its oxides can be best prepared for an iron determination by dissolving in nitric acid, although treatment of the metal with hydrochloric acid, followed by the addition of hydrogen peroxide, has been used. Uranium tetrafluoride containing iron may be dissolved in dilute acid after heating with ammonium carbonate,¹ after fusion with boric acid,^{2,3} or after fusion with ammonium oxalate.^{4,5,41} It may be dissolved with ammonium hydroxide and hydrogen peroxide, followed by acidification.⁶ Direct ignition of uranium tetrafluoride or of uranium metal to U_3O_8 and solution of the oxide in nitric acid have been shown by the National Bureau of Standards to be satisfactory for the determination of traces of iron.

1.2 Methods of Separation. (a) Precipitation. (1) Alkaline Peroxide. Treatment of samples with strong sodium hydroxide and a strong oxidant serves to separate iron from arsenic, tungsten, aluminum, phosphorus, molybdenum, vanadium, and chromium,^{7,25} and, when sodium peroxide is present, from uranium as well.

(2) Carbonate Separation. The classic separation of iron from uranium by precipitation with ammonium hydroxide-ammonium carbonate solution⁷ has been used. These reagents precipitate iron as the hydrated oxide along with the hydroxides or basic carbonates of aluminum, manganese, and some chromium, whereas uranium remains in solution. Sodium carbonate has also been employed.⁸

Separation from uranium and subsequent determination of the iron by the use of either ammonium carbonate or sodium carbonate have been described.⁸ It has been the experience of some laboratories that the ammonium carbonate-ammonium hydroxide method does not completely separate the iron from uranium because some iron tends to peptize and run through the filter paper.

(3) Pyridine Separation. Iron is completely separated from copper, cadmium, nickel, zinc, and cobalt by the addition of pyridine to a solution slightly acid with HCl. The final solution should be 0.3M in pyridinium chloride at a pH of about 5.2. Under these conditions lead is completely coprecipitated with iron. Furman, Haight, and McDuffie,⁹ in a modification of earlier work by Lingane and Kerlinger,¹⁰ have incorporated this separation of iron in a procedure for the polarographic determination of traces of impurities in uranium. This procedure is given in the chapter on electrolytic separation methods.

(4) Cupferron Separation. Cupferron (ammonium salt of nitroso-phenylhydroxylamine), which forms an acid-insoluble inner salt with iron, has been used extensively as a precipitating agent for this element.^{7,11,25} Although the number of elements partially or completely precipitated by this reagent from cold 10 per cent sulfuric acid solution is large, cupferron affords a means of separation of iron from aluminum, beryllium, chromium, phosphorus, boron, manganese, cobalt, nickel, zinc, and sexivalent uranium.

A number of the ions that are precipitated along with iron by this reagent (columbium, tantalum, titanium, vanadium, zirconium, etc.) may be removed by the ammonium sulfide-ammonium tartrate precipitation of iron.

The voluminous precipitate of iron cupferrate shows a tendency to occlude sexivalent uranium. Therefore, this method is not to be recommended for the removal of large amounts of iron prior to the determination of traces of uranium.

The precipitate of iron cupferrate is converted to hydrated ferric oxide by washing on the filter with hot ammonia solution.¹¹ The same technique dissolves the precipitate of copper cupferrate, thus affording a separation of iron and copper.

Bricker and Furman¹² have shown that the cupferron precipitation cannot be used for the quantitative recovery of less than milligram amounts of iron. The authors indicated that cupferron fails to precipitate approximately 0.2 mg of iron from a solution containing 5.7 g of uranium in 50 ml of a solution that contains 5 ml of H₂SO₄. They recommend the removal of ferric cupferrate from sulfuric acid solution by extraction with an immiscible solvent, such as diethyl ether or amyl acetate. This procedure is given below in Sec. 1.2b. Other

organic compounds, such as 8-hydroquinoline, have been used for the separation of iron, but, like cupferron, they are not specific.

(b) Solvent Extraction. (1) Extraction of Ferric Chloride. Extraction of ferric chloride from HCl solution by diethyl, diisopropyl, or dichloroethyl ether has proved to be an excellent method for the removal of most of the iron from solutions to be analyzed for other elements.^{7,13,25} Various authors have presented methods for ensuring the quantitative removal of iron from such solutions.¹⁴⁻¹⁶

(2) Extraction of Iron 8-Hydroxyquinolate (Oxinate). 8-Hydroxyquinoline (oxine) yields water-insoluble complexes with a large number of common cations, including uranium, iron, aluminum, lead, bismuth, cobalt, nickel, copper, and indium. Moeller¹⁷ found, upon agitation of aqueous solutions of certain metallic salts with chloroform solutions of oxide, that the completeness of extraction of the various organic complexes is a function of the pH of the aqueous solution. Lavollay has used an extraction method for iron in biological material.¹⁸

Rowlands¹⁹ and Smales²⁰ were able to show that this reagent may be used to separate traces of iron from uranium and to estimate the iron. The separation method of Smales is not affected by the presence of large amounts of ammonium sulfate in the solution.²¹ This method has been used to remove traces of iron prior to the determination of uranium.²² Since the oxine separation is used in connection with a colorimetric method for the determination of iron, it is discussed in somewhat more detail in the section on colorimetric methods for iron determinations.

(3) Extraction of Iron Cupferrate. The removal and recovery of small amounts of iron by the solvent extraction of iron cupferrate²³ have been accomplished. Several organic solvents have been used to effect the separation.

Bricker and Furman¹² have shown ferric cupferrate to be extracted quantitatively with diethyl ether from sulfate solutions containing large amounts of hexavalent uranium. A comparison of results with other methods is shown in Table 16.1. Amyl acetate and similar esters may be used in place of ether. Iron may be recovered from these solvents by extraction with 6N nitric acid.

The use of chloroform as the solvent has been preferred in some laboratories because of the danger of extraction of small amounts of uranium, especially in the presence of traces of nitrate, by the ether. The high density of chloroform relative to the density of the aqueous layer allows some simplification of the extraction procedure, although the rapid decomposition of cupferron in chloroform is a disadvantage. When chloroform is used as the solvent in this extraction, the iron is

recovered by evaporation of the chloroform and the destruction of cupferron, which is caused by oxidation with sulfuric and nitric acids or by ignition.

Procedure for Cupferron Extraction.¹² The solution containing iron and uranium is treated with ~1.3 ml of H_2SO_4 and evaporated to fumes of SO_3 to decompose any nitrates. The sulfuric acid solution is then diluted to 10 ml and transferred to a separatory funnel. Two or three

Table 16.1—Separation of Iron from Uranium*

Sample	Cupferrate extraction, ppm		No separation, ppm		Electrolytic separation, ppm	
1	175	177	187	187	190	190
2	88.0	90.0	97.5	96.6	98.7	94.1
3	600	546	645	648	632	
4	736	746	752	755	736	748

*Iron determination with 1,10-phenanthroline. The double columns represent the results obtained on two separate analyses of the samples.

milliliters of an aqueous solution of 5 per cent cupferron is added, and the cupferrate complexes are extracted with 10 ml of diethyl ether. The aqueous layer is drained into another separatory funnel containing 10 ml of diethyl ether. The ether in the first funnel is then washed with two 5-ml portions of water, and the washings are added to the contents of the second funnel. After extraction with the second portion of ether, the aqueous layer is discarded. The second ether layer is washed twice with 5-ml portions of water and added to the first ether extract. The iron is recovered from the combined ether extracts by shaking with two 10-ml portions of 6N HNO_3 and one 10-ml portion of water. The aqueous layers are combined and partially evaporated, and the iron is precipitated as hydrous ferric oxide. The iron may then be redissolved in a suitable acid and determined by one of the methods described below.

(c) Electrolysis. A rapid quantitative separation of iron from aluminum, titanium, zirconium, phosphorus, vanadium, and uranium is obtained by deposition of the iron in a mercury cathode from 1N H_2SO_4 solution.^{9, 24, 25} A detailed discussion of this technique is presented in the chapter on electrolytic separation methods.

After the distillation of the mercury and the solution of the residue in acid, the iron may be separated from cadmium, nickel, cobalt, copper, and zinc by precipitation with pyridine and determined colorimetrically.⁹ The separation is quantitative, as shown in Table 16.1.

Chromium, molybdenum, and manganese are deposited in the mercury very slowly, if at all, from solutions containing large amounts of uranium, so that a partial separation of iron from these elements is possible.⁹ However, from uranium-free solutions or from solutions containing 20 mg of uranium, or less, per milliliter, the chromium and most of the manganese and molybdenum are deposited quantitatively in a reasonable time (see the chapter on electrolytic separation methods). These elements will therefore accompany the iron from such solutions.

Table 16.2—Comparison of Colorimetric Methods for Determination of Iron

Reagent	Ion complexed	Optimum range, $\gamma/100$ ml	Wave-length, $m\mu$	Interfering ions
1,10-Phenanthroline	Fe(II)	20–400	505	Cu, Ni, Co, SiO_3 , oxalate NO_2
2,2'-Bipyridine	Fe(II)	30–600	522	Cu, Ni, Co
Dimethylglyoxime	Fe(II)	25–500	530	Cr
Disodium-1,2-dihydroxy benzene-3,5-disulfonate	Fe(III)	40–200	480	Cr, V, Ti, Mn, SiO_3
8-Hydroxyquinoline	Fe(III)	50–400	436	V, F, oxalate, citrate
Salicylic acid	Fe(III)	200–3,000	530	PO_4 , F, citrate, oxalate, malonate, tartrate

A large number of colorimetric methods have been used on the Project for the determination of traces of iron. Table 16.2 indicates the optimum range for an optical path of 1 cm.

1.3 Determination of Iron. In the absence of interfering ions the precipitate formed by treatment with ammonium hydroxide, ammonium hydroxide–ammonium carbonate, or cupferron may be ignited to the oxide Fe_2O_3 .

A large number of satisfactory volumetric methods for the determination of iron are available. Dichromate, permanganate, or ceric ion may be used to oxidize ferrous ion in titrations to either potentiometric or visual end points. Of the numerous reducing agents available, stannous chloride and the Jones reductor have been the most widely used.

Iodometric titration of iron may be performed after the removal of uranium by carbonate separation.²⁶ Chromium does not interfere.

Spectrographic methods have proved most useful in determining iron. The limit is 1 ppm in commercial U_3O_8 with the use of the carrier-distillation method.²⁷ The methods employed are described in the chapter on spectrochemical methods.

Direct determination of iron with such reagents as 1,10-phenanthroline, 2,2'-bipyridine, and dimethylglyoxime are quite useful when iron alone is to be determined. The use of dimethylglyoxime is preferable when iron must be determined in the presence of large amounts of quadrivalent uranium but not in hexavalent uranium.

However, when it is desirable to determine vanadium, titanium, and iron, a cupferron separation prior to the colorimetric determination may be necessary. When copper, cadmium, zinc, cobalt, and nickel are to be determined, the preferred procedure consists in the electrolytic deposition of these metals into mercury, removal of the mercury by distillation, and the pyridine separation of iron (and lead), followed by colorimetric determination of the iron and polarographic estimation of the other metals.

(a) Volumetric Methods. A great many satisfactory volumetric methods for iron are known. In many cases these methods contain only minor modifications of procedures described in standard references and texts, and therefore they will not be reviewed.^{7,13,28}

(1) Iodometric Methods. The method of oxidation of potassium iodide by ferric ion and the titration of the liberated iodine with sodium thiosulfate^{13,16} was used. The latter element is usually removed adequately by a single carbonate separation. Chromium does not interfere.²⁶

Procedure.¹⁶ The sample, which should contain 10 to 40 mg of iron, is treated with 6N NH_4OH until a slight precipitate is formed, which is redissolved in 8N HNO_3 . This solution is poured, with stirring, into a 250-ml beaker containing enough ammonium carbonate-ammonium hydroxide solution (2.5 per cent ammonium carbonate in 3N NH_4OH) to give 3 to 4 mg of ammonium carbonate per milligram of uranium in the sample. The solution is heated to 90°C and digested for 4 min, after which it is filtered and washed five times with the ammonium carbonate-ammonium hydroxide solution.

The washed precipitate is dissolved in nearly boiling 0.1N to 0.2N HCl , and the solution is collected in a flask. The filtrate is allowed to cool to room temperature, 5 g of KI is added, and the solution is then allowed to stand in the dark for 2 min. The sides of the flask are washed down, and the solution is titrated rapidly with 0.02N $\text{Na}_2\text{S}_2\text{O}_3$, the solution being gently swirled. Within 1 ml of the end point starch solution is added, and the sample is titrated to the disappearance of the blue color.

(b) Colorimetric Methods. Colorimetric reagents for iron may be divided into two groups, according to whether they react with ferrous iron or ferric iron. Among the reagents of the first group that have been used are 1,10-phenanthroline,²⁹ dimethylglyoxime,³⁰ 2,2'-bipyri-

dine,³¹ and thioglycolic acid.³² In the second group are disodium catecholdisulfonate (Tiron),³³ salicylic acid,³⁴ ammonium thiocyanate,⁷ and 8-hydroxyquinoline.¹⁸ Modifications of the classic thiocyanate

Table 16.3—Interferences in the Determination of Iron with 1,10-Phenanthroline

Ions	Added as	Ion/iron weight ratio for 3% error in optical density	Type of interference*
Cations			
U(VI)	UO ₂ Cl ₂	12,000	I
Cr(III)	K ₂ Cr ₂ (SO ₄) ₄	64	I
Cr(VI)	K ₂ CrO ₄	2	D
Mo	MoO ₃ + NaOH	4	D
V	V ₂ O ₅ + NaOH	2.4	D
Cu	CuSO ₄	1.2	D
Zn	ZnCl ₂	4.8	D
Al	Al ₂ (SO ₄) ₃	120	I
Mg	MgCl ₂	80	I
Ca	CaCl ₂	400	I
Sn	SnCl ₂	32	I
Ti	TiO ₂ + K ₂ S ₂ O ₇ (fusion)	4	I
Ni	NiCl ₂	0.8	D
Mn	MnCl ₂	16	D
Cd	CdCl ₂	16	D
U(IV)	UCl ₄	80	I
Anions			
Cl	NaCl	†	
PO ₄	Na ₂ HPO ₄	0.8 and 1,600	D
NO ₃	NaNO ₃	>20,000	D
C ₂ O ₄	Na ₂ C ₂ O ₄	4	D
SiO ₃	NaSiO ₃	0.8	D
SO ₄	Na ₂ SO ₄	8,000	I
F	KHF ₂	80	D
CH ₃ COO	CH ₃ COONa	8	D
C ₆ H ₅ O ₇	K ₃ C ₆ H ₅ O ₇ (citrate)	400	D
ClO ₄	NaClO ₄ ·H ₂ O	1,200	D
NO ₂	NaNO ₂	20	D
C ₄ H ₄ O ₆	K ₂ C ₄ H ₄ O ₆ (tartrate)	4,000	D
SO ₃	Na ₂ SO ₃	8	D

* I, interfering ion causes increase in optical density; D, interfering ion causes decrease in optical density.

† No interference.

method were used.³⁵⁻³⁷ The reagents that react with ferrous ion are probably to be preferred because anions such as fluoride, phosphate, and oxalate, which form stable complexes with ferric ion in acid solu-

tion, do not interfere in color development with the reagents for ferrous iron. Iron is readily reduced to the bivalent state by hydroxylamine.

(1) 1,10-Phenanthroline. 1,10-Phenanthroline has proved to be the most satisfactory of the reagents tested for the determination of trace amounts of iron, the optimum color being produced by 20 to 400 γ of iron in 100 ml of the solution with 1-cm absorption cells.

It has been reported that the interference of zinc, cadmium, and mercury can be diminished by using a large excess of reagent.³⁵ Precipitation of bismuth phosphate when nitric acid solutions containing these ions are neutralized may be prevented by the addition of citrate ions.³⁸ One milliliter of 10 per cent sodium citrate will hold about 80 mg of bismuth phosphate in 25 ml of solution. Although Table 16.3 indicates that citrate interferes, this occurs only if it is present before reduction of the iron. If the citrate is added after reduction to iron(II), no interference results.

Table 16.3, taken from the work of Lee, Weaver, and Clewett,³⁹ shows the ratio of impurity to iron necessary to cause an error of 3 per cent in the optical density due to 125 γ of iron.

A large number of modifications of this method have been adopted. Fassel's procedure⁴⁰ may be considered typical.

Procedure. After the sample has been dissolved in HNO_3 , the solution is evaporated to a syrupy consistency and diluted with water. The pH is then adjusted to about 3 (with pH indicator paper) with dilute NH_4OH and HCl added dropwise. At the right pH the yellow precipitate of ammonium diuranate just dissolves. The solution is transferred to a 100-ml volumetric flask, and 1 ml of 10 per cent hydroxylamine hydrochloride and 10 ml of 0.1 per cent 1,10-phenanthroline solution are added. The solution is mixed well, diluted to 100 ml, and again mixed. It should be noted that 10 ml of 1,10-phenanthroline solution is required for 500 γ , or less, of iron. When larger quantities of iron are present, the sample should be further diluted, and more reagent added. Dilution should be sufficient to bring the iron concentration within the limits of the calibration curves. The solutions should be permitted to stand for at least 20 min before readings are taken.

The iron concentration is determined by spectrophotometric measurement against a reference solution containing the same amount of uranyl ion per 100 ml. The reading is made at 515 $\text{m}\mu$. At this wavelength maximum absorption is obtained for the ferrous 1,10-phenanthroline complex.

(2) 2,2'-Bipyridine. Applications of the method involving 2,2'-bipyridine have been made.^{37, 41-43} Mellon,⁴⁴ who has described this re-

agent in detail, showed that the reddish-purple color has its maximum absorption at 522 m μ . Uranyl ion absorbs very little light at this wavelength. Anderson et al.⁴⁵ have investigated the effect of uranium at 510 m μ .

A variation of pH between 3 and 9 does not influence the intensity of the iron-bipyridine color. In the presence of large amounts of uranium, however, the pH must be maintained below 4.5 to prevent the precipitation of uranium. The addition of a considerable excess of hydroxylamine before the pH is adjusted usually prevents precipitation.

Moss,⁴⁴ who has presented a comprehensive study of the effect of other ions, has shown that the most significant interferences are those of cobalt, nickel, and copper, from which the iron may be separated by precipitation with ammonia.

Procedure.⁴⁶ A sample weighing from 1 to 2.5 g is cleaned in hot HNO₃ (1 to 3), rinsed in water and then in acetone, dried, weighed, and dissolved in 10 ml of HCl. When the reaction has ceased, 30 per cent H₂O₂ is added dropwise to oxidize the uranium. The solution is then boiled for 3 to 5 min. The solution is diluted to 100 ml, and an aliquot corresponding to 0.50 g of sample is taken. To this aliquot 10 ml of 10 per cent hydroxylamine hydrochloride and 30 ml of water are added. The pH of the solution is adjusted to 3.8, with 10 per cent NH₄OH used for final adjustment. To the solution is added 2.0 ml of 0.2 per cent 2,2'-bipyridine, and the volume is brought to 125 ml in a graduated cylinder and mixed well. The transmittancy of the solution is measured against an iron-free uranium solution of the same concentration at 525 m μ .

(3) Dimethylglyoxime. Dimethylglyoxime yields a pink color with ferrous ion in a solution made basic with ammonia. Since intensity of the color increases with increasing pH, careful control of the hydrogen-ion concentration is essential. Baker, House, and Susano⁴⁷ recommend that the pH be kept between 9.4 and 9.5. The color intensity is increased by the addition of a small amount of copper sulfate, although this increase appears to be independent of the copper concentration. The colored complex is more stable in solutions containing large amounts of ammonium chloride, but high concentrations of the salt decrease the solubility of dimethylglyoxime in the solution.

The absorption of light by the colored complex has been shown to follow Beer's law. The complex exhibits maximum light absorption at 530 m μ .

This reagent is particularly suited for the determination of iron in the presence of large amounts of uranium(IV), since U(OH)₄ is precipitated during adjustment of the pH and may be removed, without

appreciable error, by centrifuging. The presence of aluminum, however, results in a voluminous precipitate of $\text{Al}(\text{OH})_3$, which carries down significant amounts of the colored complex. The error has been

Table 16.4—Interferences in the Determination of Iron with Dimethylglyoxime

Ions	Added as	Ion/iron weight ratio for 3% error in optical density	Type of interference*
Cations			
U(VI)	UO_2Cl_2	400	I
Cr(III)	$\text{K}_2\text{Cr}_2(\text{SO}_4)_4$	0.3	D
Cr(VI)	K_2CrO_4	0.4	D
Mo	$\text{MoO}_3 + \text{NaOH}$	16	
V	$\text{V}_2\text{O}_5 + \text{NaOH}$	4	I
Cu	CuSO_4	40	I
Zn	ZnCl_2	400	I
Al	$\text{Al}_2(\text{SO}_4)_3$	16	Precipitation
Mg	MgCl_2	160	
Ca	CaCl_2	400	I
Sn	SnCl_2	80	D
Ti	$\text{TiO}_2 + \text{K}_2\text{S}_2\text{O}_7$ (fusion)	24	D
Ni	NiCl_2	80	I
Mn	MnCl_2	3,200	I
Cd	CdCl_2	8,000	I
U(IV)	UCl_4	†	
Anions			
Cl	NaCl	†	
PO_4	Na_2HPO_4	400	D
NO_3	NaNO_3	†	
C_2O_4	$\text{Na}_2\text{C}_2\text{O}_4$	†	
SiO_3	NaSiO_3	32	D
SO_4	Na_2SO_4	†	
F	KHF_2	1,600	D
CH_3COO	CH_3COONa	†	
$\text{C}_6\text{H}_5\text{O}_7$	$\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ (citrate)	1,600	D
ClO_4	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	> 24,000	
NO_2	NaNO_2	400	D
$\text{C}_4\text{H}_4\text{O}_6$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ (tartrate)	1,200	D
SO_3	Na_2SO_3	200	D

*I, interfering ion causes increase in optical density; D, interfering ion causes decrease in optical density.

†No interference.

shown to be less than 3 per cent when the aluminum/iron ratio is less than 16.

Table 16.4, taken from the work of Lee, Weaver, and Clewett,³⁹ shows the ratio of impurity to iron necessary to cause an error of

3 per cent in the optical density due to 125 γ of iron. Chromium, added as either chromate or chromic ion, is the major interfering element. Although the procedure of Baker, House, and Susano includes nitrate removal by fuming with sulfuric acid, the data of Lee, Weaver, and Clewett show no need for this operation.

Procedure.⁴⁷ A known amount of UCl_4 is dissolved in water. Three milliliters of HCl is added, and the solution is diluted to 250 ml. A suitable aliquot (20 to 150 γ of iron) is pipetted into a 50-ml graduated conical centrifuge tube. To the solution are added 1 ml of CuSO_4 solution (0.25 mg of copper per milliliter), 2 ml of hydroxylamine solution (0.1 g of hydroxylamine hydrochloride per milliliter), 20 ml of NH_4Cl solution (0.2 g of NH_4Cl per milliliter), and 1 ml of dimethylglyoxime solution (saturated solution in 95 per cent ethyl alcohol). The solution is mixed thoroughly, 5 ml of NH_4OH is added, and the solution is made up to the 50-ml mark with water. The solution is mixed, and after 10 min it is centrifuged at 2,500 rpm. The supernatant liquid is decanted, and the transmittancy is measured at 525 $\text{m}\mu$ against a blank carried through the whole procedure. The iron content is obtained from a transmittancy-concentration curve.

(4) Disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron). The Yoe and Jones³³ reagent for iron, disodium-1,2-dihydroxybenzene-3,5-disulfonate, gives a cherry-red color with ferric iron in basic solution. These authors recommend the use of a solution buffered with phosphate at pH 9.5 or with carbonate at pH 9.8. Widmer,⁴⁸ who investigated the application of this reagent to iron in the presence of uranium, found that uranium was precipitated from the solution buffered with phosphate; accordingly, he recommended the use of a carbonate buffer. He also indicated that the reproducibility and stability of the color would be improved if the pH were lowered to 8.6. This change results in a slight decrease in sensitivity. Color intensity was shown to be independent of the reagent concentration, provided the reagent is present in a molar excess of more than 3 to 1.

Lee, Weaver, and Clewett³⁹ made a comparison of this reagent with 1,10-phenanthroline and with dimethylglyoxime. Table 16.5 shows the ratio of impurity to iron necessary to cause an error of 3 per cent in the optical density due to 125 γ of iron.³⁹ Uranium interferes much more seriously with this reagent than with either dimethylglyoxime or 1,10-phenanthroline. Silicate also exhibits strong interference and must be removed prior to the determination.

Procedure.³⁹ A 10-ml aliquot containing 30 to 500 γ of iron is transferred to a 25-ml volumetric flask. One milliliter of 0.05M Tiron solution is added, and the pH is adjusted to 8; then 10 ml of a carbonate buffer solution (prepared by dissolving 20 g of NaHCO_3 in 1 liter of water and adjusting the pH to 8.6 by the addition of Na_2CO_3)

is added. The contents of the flask are diluted to the mark and mixed thoroughly. The optical density of the solution is measured at $480\text{ m}\mu$. The iron content is obtained from a previously constructed calibration curve.

Table 16.5—Interferences in the Determination of Iron with Disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron)

Ions	Added as	Ion/iron weight ratio for 3% error in optical density	Type of interference*
Cations			
U(VI)	UO_2Cl_2	8	I
Cr(III)	$\text{K}_2\text{Cr}_2(\text{SO}_4)_4$	3.2	I
Cr(VI)	K_2CrO_4	0.8	D
Mo	$\text{MoO}_3 + \text{NaOH}$	4	I
V	$\text{V}_2\text{O}_5 + \text{NaOH}$	0.8	I
Cu	CuSO_4	5.6	I
Zn	ZnCl_2	40	I (precipitation)
Al	$\text{Al}_2(\text{SO}_4)_3$	3.2	D
Mg	MgCl_2	160	I
Ca	CaCl_2	8	I (precipitation)
Sn	SnCl_2	10	D (precipitation)
Ti	$\text{TiO}_2 + \text{K}_2\text{S}_2\text{O}_7$ (fusion)	0.08	I
Ni	NiCl_2	16	D
Mn	MnCl_2	0.6	I
Cd	CdCl_2	4	I (precipitation)
U(IV)	UCl_4	12	I
Anions			
Cl	NaCl	†	
PO_4	Na_2HPO_4	4–1,200	D
NO_3	NaNO_3	†	
C_2O_4	$\text{Na}_2\text{C}_2\text{O}_4$	†	
SiO_3	Na_2SiO_3	0.8	D
SO_4	Na_2SO_4	†	
F	KHF_2	640	D
CH_3COO	CH_3COONa	64	D
$\text{C}_6\text{H}_5\text{O}_7$	$\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ (citrate)	†	
ClO_4	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	†	
NO_2	NaNO_2	24	D
$\text{C}_4\text{H}_4\text{O}_6$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ (tartrate)	†	
SO_3	NaSO_3	8	D

*I, interfering ion causes increase in optical density; D, interfering ion causes decrease in optical density.

†No interference.

(5) 8-Hydroxyquinoline. The extraction separation of iron from uranium and the subsequent determination of iron with 8-hydroxyquinoline have been used.

A method proposed by Smales²⁰ has been used to separate iron from uranium in three-fourths saturated ammonium sulfate solution.^{21,22} A method recommended later by Rowlands¹⁹ may be used for this separation, but it is slightly more difficult of application.

Smales, in an extension of the work of Moeller,¹⁷ was able to show that the extraction of ferric 8-hydroxyquinolate from solutions buffered with ammonium acetate was complete if the pH of the aqueous phase was maintained between 2.8 and 4.3. Inasmuch as no uranium 8-hydroxyquinolate is extracted from such solutions below pH 3.1, the complete separation of iron from uranium is feasible.

Anions that form complexes with either uranium or iron (i.e., fluoride, oxalate, or citrate) must be absent. Rowlands¹⁹ has shown that as much as 0.1 mg of aluminum, bismuth, cobalt, nickel, or copper has negligible effect up to pH 2, whereas vanadium interferes. The extraction of iron is not complete at this pH. A loss of 20 γ occurs, but it is generally of the order of magnitude of the blank. In the absence of interfering ions the method gives results that are accurate within 3 per cent.

Procedure.²⁰ A 1-g sample is dissolved in HNO_3 (1 to 1). Ammonium hydroxide is added until a permanent precipitate forms, which is redissolved with 4 to 5 drops of HNO_3 . The solution is diluted to 20 ml, and the pH is adjusted to 2 with 0.1N H_2SO_4 or 0.1N NH_4OH (by means of a glass electrode). The solution is then transferred to a 50-ml separatory funnel and is shaken vigorously with a 10-ml portion of 0.01M 8-hydroxyquinoline in chloroform. The layers are allowed to separate, and the solvent layer is filtered through a Whatman No. 40 filter paper into a 50-ml stoppered cylinder. The pH of the aqueous layer is readjusted to pH 2 and reextracted with another 10-ml portion of the reagent. The solvent layer is separated and filtered as before. (Two extractions are usually sufficient.) The extracts are made up to 30 ml, and the transmittancy is measured at 436 $\text{m}\mu$ against a reagent blank. The iron content is determined from a transmittancy-concentration curve.

(6) Salicylic Acid. The intense red color formed by the addition of salicylic acid to a weakly acid solution containing iron may be used for the estimation of this element.^{30,34,49} The color intensity is a function of the pH of the solution, but it is little affected between pH 3.5 and 4.0. Control of the pH at 3.7 ± 0.2 is provided by the use of an acetate buffer. The color is dependent on the concentration of buffer and reagent, as well as on pH, so that the amount of reagents added must be carefully controlled. The wavelength of maximum absorption was found to be about 490 $\text{m}\mu$. Inasmuch as absorption due to sexivalent uranium is still appreciable in this region,³⁴ it is better

to measure the transmittancy at 530 $m\mu$.⁴⁹ The optimum range of iron concentrations when 1-cm comparison cells are used is 0.2 to 3.0 mg per 100 ml.

If the procedure given below is used, no interference is shown by calcium, manganese, zinc, and aluminum when these ions are present to the extent of 100 times the amount of iron. The interference of chromium(III) is negligible if it is present to the extent of less than 10 times the iron concentration. The interference of uranium is negligible if less than 6 mg per milliliter is present in the solution used for color comparison.

Anions capable of forming stable complexes with ferric ion show strong interference with this method. Thus phosphate, fluoride, tartrate, malonate, citrate, and oxalate must be removed prior to the determination. The interference of fluoride may be avoided by the addition of an equivalent amount of aluminum.⁴⁹ An accuracy of 5 per cent is claimed.

Procedure.⁴⁹ An aliquot of the solution containing 100 to 500 γ of iron(III) is transferred to a 25-ml volumetric flask. Ammonium hydroxide (1 to 9) is added drop by drop until precipitation begins, and then 10 ml of buffer solution (30 g of sodium acetate and 25 g of sodium salicylate in 200 ml of glacial acetic acid, diluted to 500 ml with water) is added. The sample is diluted to the mark with distilled water and mixed well. The transmittancy is measured at 530 $m\mu$ against a blank containing 10 ml of buffer per 25 ml in the comparison cell. The iron content is obtained from a transmittancy-concentration curve.

2. COBALT

2.1 Methods of Solution. Uranium metal to be analyzed for cobalt may be dissolved rapidly by attack with hydrochloric acid followed by nitric acid, or by ignition to U_3O_8 followed by solution in dilute nitric acid.

Boric acid fusion of UF_4 may be employed. Graphite ash may be dissolved in HCl.

2.2 Methods of Separation. Cobalt may be separated from uranium, aluminum, molybdenum, vanadium, and chromium by precipitation with an excess of sodium hydroxide, sodium carbonate, and sodium peroxide.⁷ This precipitate may be examined spectrographically for cobalt, indium, scandium, titanium, zirconium, and hafnium. The limit of spectrographic determination of the element in this precipitate is 5 γ of cobalt.⁵⁰

Cobalt, along with iron, copper, nickel, chromium, zinc, and cadmium, is deposited quantitatively from a sulfuric acid solution into a

mercury cathode and is thus separated from uranium, aluminum, and the alkali metals (see references 7, 24, 25, 51, 52). Cobalt may be recovered as the oxide on distillation of the mercury and may be determined polarographically or colorimetrically in the residue.⁵³

2.3 Methods of Determination. Determination of cobalt in uranium ores has been made in the conventional manner⁷ by precipitation with 1-nitroso-2-naphthol.⁵⁴

Since most determinations of cobalt involved small amounts, the colorimetric method using tetraphenylarsonium chloride has been employed most often for cobalt determination.

Polarographic methods have been applied to the determination of cobalt in the presence of nickel. In the procedure used the waves of zinc and cobalt overlap, so that, if zinc is present, the cobalt is determined by a colorimetric method.⁹

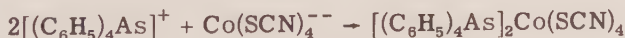
Table 16.6—Optimum Range for Determination of Traces of Cobalt

Method	Range	Interference
Colorimetric:		
Tetraphenylarsonium chloride	5–120 γ	Cu(II), Mo(III)
Polarographic:		
Pyridine medium	10–200 γ	Zn
Spectrographic:		
Copper spark	0.050–5 γ	
Carrier distillation	Limit 1 ppm	

Spectrographic methods have been widely used for detection and determination of cobalt. These methods are discussed in the chapter on spectrochemical methods. Table 16.6 indicates the sensitivity of the various methods of determination of cobalt.

(a) **Colorimetric Methods.** Of the various colorimetric methods available^{55–57} for the determination of trace amounts of cobalt, one is the tetraphenylarsonium chloride method.⁵⁶ Sodium diethyldithiocarbamate has been used for the determination of cobalt in nickel.⁵⁷

(1) **Tetraphenylarsonium Chloride Method.** The method developed by Potratz⁵⁶ is based on the formation of a blue chloroform-soluble reaction product between the cobalt thiocyanate complex and an aryl “onium” ion such as tetraphenylarsonium chloride. The reaction involved is as follows:



A spectral transmittancy curve for the complex in chloroform is shown in Fig. 16.1, and a typical transmittancy-concentration curve is shown in Fig. 16.2. This method has been used for the determination of cobalt in a large variety of materials, including nickel oxide, ores, steel, and uranium metal and compounds.^{9,58,59}

The thiocyanate complexes of ferric iron, cupric copper, and trivalent molybdenum will react with tetraphenylarsonium ion to give colored chloroform-soluble compounds. Interferences due to ferric and uranyl ion are prevented by complexing these ions with fluoride. Interference by cupric ion is prevented by reduction to the cuprous state. Bismuth, which can be determined by tetraphenylarsonium chloride under other conditions, does not interfere.

The chloroform solution of the tetraphenylarsonium cobaltothiocyanate complex is quite stable, showing a decrease in transmittancy of only 0.4 to 0.6 per cent after standing in the dark for 24 hr.

The method is most applicable in the range from 10 to 200 γ of cobalt. Approximately 95 per cent recovery was obtained with synthetic samples containing 1 to 20 ppm of cobalt in uranium solutions.

Procedure.⁵⁹ A weighed sample of suitable size is dissolved in nitric acid, and excess acid is expelled by evaporation of the solution nearly to dryness. The solution is diluted and transferred to a large separatory funnel with a final volume of approximately 200 ml. Eight milliliters of 50 per cent potassium thiocyanate solution, 5 g of ammonium fluoride, 2 ml of 0.05M tetraphenylarsonium chloride solution, and 8 ml of chloroform are added, and the mixture is shaken vigorously. The chloroform layer is drawn off into a small separatory funnel. This extraction is repeated three times by using 4-ml portions of chloroform, with the addition of 1 to 2 ml of 0.05M tetraphenylarsonium chloride solution before each extraction. The combined chloroform extracts contained in the small separatory funnel are shaken with 10 ml of water to which about 0.1 g of ammonium fluoride, 2 ml of 50 per cent potassium thiocyanate, and 1 ml of 0.05M tetraphenylarsonium chloride solution have been added. A yellow-green color in the chloroform layer indicates the presence of copper. To reduce the copper to the cuprous state, 1 ml of 10 per cent potassium iodide solution is added, and the mixture is shaken vigorously. The iodine liberated by the oxidation of the potassium iodide is now removed by shaking with 1 ml of 10 per cent sodium thiosulfate solution. The blue chloroform layer (colorless if cobalt is absent) is filtered through a small dry filter paper, and the filtrate is caught in a 25-ml volumetric flask. The aqueous layer remaining in the small separatory funnel is shaken once more with 4 to 5 ml of chloroform and 1 ml of 0.05M tetraphenylarsonium chloride solution. If extraction is complete, the chloroform layer will remain colorless. The

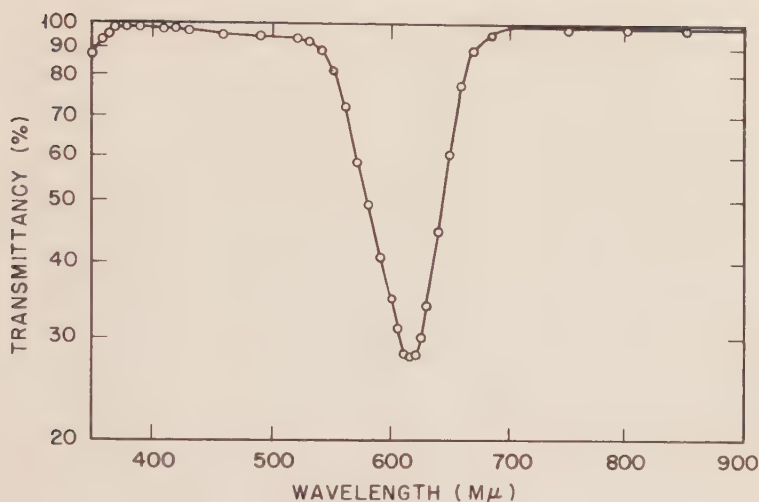


Fig. 16.1—Spectral transmittancy curve for the tetraphenylarsonium cobaltothiocyanate compound.

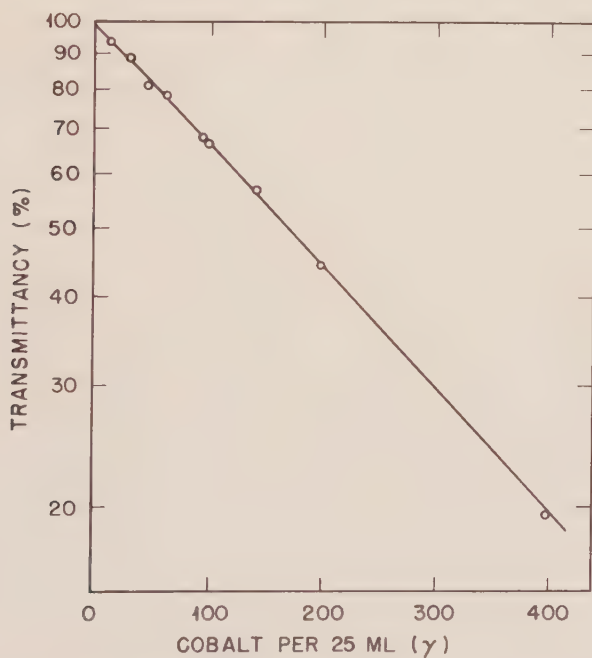


Fig. 16.2—Transmittancy-concentration curve for the determination of cobalt with thiocyanate and tetraphenylarsonium chloride, measured in 25 ml of chloroform at 615 mμ with a Coleman model 10S spectrophotometer with a 30-mμ slit and cylindrical cells.

last portion of chloroform extract is filtered and added to the flask, the filter paper is washed with sufficient chloroform to fill the flask to the mark, and the solution is mixed well by shaking. The transmittancy of the solution is measured at 615 $m\mu$ against a blank carried through the procedure.

(2) Sodium Diethyldithiocarbamate. The determination of traces of cobalt in nickel has been accomplished by the use of sodium diethyldithiocarbamate, which forms colored precipitates with iron, manganese, copper, cobalt, and nickel. Iron and manganese can be removed by precipitation with ammonia. Copper is removed by electrolysis prior to the colorimetric determination. Although the reagent precipitates both cobalt and nickel from ammoniacal solution, the cobalt salt is quite soluble in carbon tetrachloride, whereas the nickel salt is only slightly soluble.⁵⁷ Extraction of the slurried precipitates, therefore, allows the partial separation of the two salts and permits the determination of cobalt. Interference of the nickel salt, due to its slight solubility, is minimized by using a blank consisting of carbon tetrachloride saturated with nickel diethyldithiocarbamate.

Beer's law is obeyed at 600 $m\mu$. The optimum range of cobalt concentration has been shown to be 50 to 250 γ of cobalt per 100 ml of carbon tetrachloride solution.⁵⁷

Procedure.⁵⁷ The weighed sample of nickel is dissolved in concentrated nitric acid. The solution is diluted and treated with ammonia until it has the distinct odor of this reagent. The solution is then filtered to remove iron and manganese. Enough 0.5N sodium diethyldithiocarbamate is added to the ammoniacal solution to allow 20 per cent excess over the amount required to precipitate the entire sample (calculated as nickel). The slurry is transferred to a separatory funnel, and the cobalt salt is extracted with five to ten 20-ml portions of carbon tetrachloride. The combined extracts are dried over calcium chloride and filtered into a volumetric flask. The carbon tetrachloride used for washing the filter paper and diluting the solution to volume is saturated with nickel diethyldithiocarbamate by shaking with the nickel salt remaining in the separatory funnel. An aliquot of the carbon tetrachloride solution is then diluted with pure carbon tetrachloride to a volume that will give a convenient spectrophotometric reading. The optical density is measured at 680 $m\mu$ against a comparison blank. This blank is prepared by diluting a saturated carbon tetrachloride solution of nickel diethyldithiocarbamate with pure carbon tetrachloride in the same ratio as the actual sample.

(b) Polarographic Method. Thanheiser and Maassen⁶⁰ and Lingane and Kerlinger¹⁰ have developed methods for the polarographic estimation of cobalt in the presence of nickel.

The method developed by Furman, Haight, and McDuffie⁹ for the determination of trace impurities in uranium uses the pyridine separation as proposed by Lingane and Kerlinger.

In the pyridine-pyridinium chloride medium, although the waves of nickel and cobalt are separated by about 0.3 volt, the wave of the latter coincides with that of zinc. Thus cobalt can be determined only in solutions in which zinc is known to be absent. Since zinc was usually present in the materials analyzed, the cobalt and zinc composite wave was used to determine the sum of cobalt and zinc, the cobalt was then measured by the tetraphenylarsonium chloride colorimetric method⁶⁶ described above, and the zinc was estimated by the difference. For further information see below, on the polarographic determination of nickel.

3. NICKEL

3.1 Methods of Separation. Separation methods used prior to nickel determination have been limited to dimethylglyoxime precipitation and electrolytic methods. Numerous separation methods are described in the literature (see references 7, 13, 61, 62). Nickel, along with copper, cobalt, manganese, iron, and zinc, is extracted with carbon tetrachloride from slightly acid solution in the form of dithiocarbamates.⁶³ This method, which also separates zinc and manganese, is carried out on an aqueous solution after a cupferron-chloroform extraction, as given under "iron." The aqueous solution from the cupferron extraction is treated with saturated ammonium citrate and hydroxide to a thymol blue end point (blue).⁶³ Sodium diethyldithiocarbamate solution (0.1 g in 5 ml of H₂O) is added, and the solution is extracted with chloroform.

Nickel may be separated from the alkalis, magnesium, the alkaline earths, aluminum, and uranium by deposition from sulfuric, phosphoric, or perchloric acids into a mercury cathode. The nickel may be recovered along with zinc, cadmium, copper, iron, cobalt, and lead by distillation of the mercury. The nickel may then be determined polarographically.⁹

3.2 Methods of Determination. The classic procedure using tartaric acid or citric acid to complex uranium, iron, bismuth, etc.,⁷ with final weighing of the nickel as nickel dimethylglyoxime or oxide, was used.^{64, 65}

A number of volumetric methods for nickel have been proposed. Procedures are available in standard reference works.^{7, 13}

Colorimetric determination of traces of nickel by treatment of nickel in an oxidizing ammoniacal solution with dimethylglyoxime⁶⁶

has been shown to be quite satisfactory for the determination of nickel in uranium solutions.⁶⁷⁻⁷⁰ For control work the comparison of the chloroform extract of the nickel dimethylglyoxime with standards has proved adequate.¹⁶

When it is necessary to determine traces of nickel along with small amounts of cadmium, zinc, copper, iron, or cobalt, the polarograph may be employed (see the chapter on electrolytic separation methods).

Spectrographic detection and estimation of nickel in a wide variety of materials has proved to be a valuable analytical method. Nickel

Table 16.7—Optimum Range of Methods for Determination of Traces of Nickel

Method	Range	Interference
Colorimetric:		
Dimethylglyoxime	5–120 γ	Cu, Pd, Co, Mn
Spectrographic:		
Carrier distillation	Limit 2 ppm	
Copper spark	0.05–5 γ	
Polarographic	< 10 γ	

may be estimated with an accuracy of 10 per cent. It is further discussed in the chapter on spectrochemical methods. Table 16.7 gives the optimum range of methods for the determination of traces of nickel.

(a) Gravimetric Methods. Of the various compounds of nickel, only two have been used extensively as weighing forms for analytical determination.^{64,65} Nickel dimethylglyoxime may be weighed as such after drying at 110 to 120°C, or it may be ignited to, and weighed as, NiO.¹³

(b) Colorimetric Methods. The characteristic wine-colored complex formed by nickel that has been treated with a strong oxidant and dimethylglyoxime in ammoniacal solution has long been used for the rapid determination of small amounts of nickel.⁶⁶ Among the oxidants proposed are lead dioxide, ammonium persulfate, bromine water, and hypochlorite. Bromine⁷¹ allows fading of the color and causes evolution of some bubbles of gas, but it has been used.^{69,70,72} Rodden and Petretic,⁶⁸ who have studied the effect of various oxidants in this reaction, recommend ammonium persulfate as forming the most stable color. The color is due to a soluble nickelic complex of dimethylglyoxime. If more than microgram amounts of nickel are present, nickel dimethylglyoxime precipitates.

Palladium interferes, as in the gravimetric method. With dimethylglyoxime, in the presence of an oxidizing agent, copper forms a purple color that has been used for the detection of traces of copper.

Amounts of manganese above 2 per cent may precipitate as brown colloidal dioxide. Titanium is precipitated by ammonia and must be removed before development of the color.

One procedure made use of this method for the determination of nickel in uranium solutions after removal of the uranium as its peroxide.⁷² Murray and Ashley⁷³ pointed out that nickel could be determined in the presence of iron by using citrate ion to hold the iron in the alkaline solution necessary for the formation of the colored complex. Dobratz⁷⁰ used citrate ion to complex uranium prior to the determination of nickel.

Though the absorption of the colored complex reaches a maximum at 420 m μ , the absorption of light is still strong at 530 m μ . Since neither iron nor uranium, in citrate solution, absorbs appreciably at wavelengths above 500 m μ , various procedures have been developed for the determination of nickel in solutions containing uranium or iron, or both.

(1) Procedure with Bromine as Oxidant.⁷⁰ Two 1-g samples are weighed into small beakers, 3 ml of HNO₃ is added, and the mixture is heated. When the sample is dissolved, the solution is heated a little longer to drive off oxides of nitrogen. It is then cooled to room temperature, and 10 ml of distilled water, 2 ml of bromine water, and 10 ml of 10 per cent citric acid solution are added. Five milliliters of NH₄OH is added to one solution, which is diluted to 50 ml with distilled water and set aside as a color reference. Five milliliters of NH₄OH and 1 ml of dimethylglyoxime solution (1 per cent in alcohol) are added to the other solution, which is diluted to 50 ml with distilled water. The color of the second solution is immediately compared with that of the color reference solution in the electrophotometer by means of the green light filter (about 525 m μ). The amount of nickel present is read directly from a standard calibration curve.

(2) Procedure with Ammonium Persulfate as Oxidant.⁶⁸ The sample is dissolved in HNO₃ and taken to dryness with 5 ml of H₂SO₄ (1 to 1). It is then taken up in a few milliliters of water, and to it are added, successively, 5 ml of 20 per cent ammonium citrate, 0.1 g of ammonium persulfate, 5 ml of NH₄OH (1 to 1), and 1 ml of dimethylglyoxime solution (1 per cent in alcohol). The solution is diluted to 25 ml and allowed to stand for 15 min. The transmittancy is measured at 520 m μ within 1 hr against a blank (containing the same amount of uranium) carried through the procedure, but with the omission of dimethylglyoxime.

Samples of dolomite⁶⁷ have been analyzed by a slight modification of the bromine oxidation procedure. Calcium is removed by precipitation as sulfate, and 1 g of citric acid is used instead of the ammonium citrate solution.

(c) Polarographic Method. Lingane and Kerlinger¹⁰ showed that, if pyridine is used to precipitate iron and chromium, then copper, nickel, and cobalt can be simultaneously determined in the filtrate by polarographic methods. Since the wave for cobalt is about 0.3 volt more negative in this solution, traces of nickel can be determined in the presence of large amounts of cobalt. Other workers have modified this procedure somewhat in order to determine simultaneously copper, nickel, cobalt, cadmium, and zinc after electrolytic deposition of these materials from uranium solutions into a mercury cathode. Their procedure is given in the chapter on electrometric methods.

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Chapter 17

MANGANESE, TECHNETIUM, AND RHENIUM

By R. W. Bane and C. J. Rodden

The chief material analyzed for manganese was uranium metal. Some determinations in alloys and other materials were also made. Technetium was of interest in fission products, but rhenium has been of only minor interest.

1. MANGANESE

1.1 Methods of Solution. Uranium metal and oxides are readily put into solution with nitric acid for manganese determination. This treatment is also satisfactory for lime, dolomite, and similar materials. Perchloric acid and peroxide have been used to dissolve alloys of manganese and uranium. With high-uranium alloys the addition of a trace of fluosilicic acid facilitates solution. It was found necessary to fume strongly with perchloric acid to avoid chloride-ion interference.

1.2 Methods of Separation. Manganese is usually determined in a separate sample by methods that do not require separation. The separation of chloride, cobalt, and chromium is necessary in certain solutions containing these elements in addition to nickel, iron, copper, and uranium. Pillsbury¹ has described a method for these separations using AgNO_3 for the removal of chloride, ZnO suspension for the removal of chromium, and an acetate-buffered solution for the removal of cobalt. Other workers have also employed a separation of the manganese from the uranium prior to its determination. After removal of the cupferrates from the uranium solution the manganese was extracted as the diethyldithiocarbamate.¹⁸

1.3 Methods of Determination. (a) Volumetric Methods. (1) Uranium-Manganese Alloys. Macro amounts of manganese are generally determined by volumetric methods involving the oxidation of the

manganese by sodium bismuthate or ammonium persulfate,¹⁻⁴ followed by titration of the permanganate formed with ferrous sulfate or sodium arsenite. The determination of manganese by the bismuthate method is generally conceded to be the most accurate analytical procedure for determination of this element in iron and steel. It is simple and rapid, and it can generally be accomplished without a previous separation. Various modifications of the volumetric methods have been used. The following procedure for uranium-manganese alloys employs the bismuthate oxidation, followed by ferrous sulfate titration. It is essentially the same as the procedure given by Scott.⁵

Procedure.^{3,5} The alloy is weighed (usually 2 to 15 g is sufficient for the determination of manganese in a uranium-manganese alloy) and then dissolved with 60 per cent perchloric acid and hydrogen peroxide. The dark solution is heated to fuming; if MnO_2 precipitates, the addition of more hydrogen peroxide will redissolve it. The clear yellow solution is then cooled and diluted to a definite volume, and aliquots of the proper size are taken. Two 100-ml aliquots are transferred with a pipet to 750-ml Erlenmeyer flasks, and 50 ml of HNO_3 and 50 ml of water are added to each flask. The solution is cooled, and the calculated (from a trial run) amount of bismuthate is added all at once. The contents of the flask are agitated briskly for 1 min, and 200 ml of cold water is added. The solution is filtered through asbestos, and the residue is washed with dilute HNO_3 (3 to 100) until the washings fail to show the slightest trace of pink. The weighed ferrous salt is placed in a 1-liter beaker, and the filtered solution is added to it. The solution is stirred thoroughly until the permanganic acid has been decolorized and all the salt has dissolved. It is immediately titrated with the standardized 0.1N potassium permanganate to a faint pink color.

(2) Materials in Solution. For solutions containing U, Fe, Cu, Cr, Ni, or Co the procedure given below employs a slight modification of the previous method in that the bismuthate oxidation is performed in sulfuric acid solution.^{1,2}

Procedure.¹ An aliquot containing no more than 50 mg of Mn is used. The manganese and chromium should be in the reduced states (Mn^{++} , Cr^{+3}). The sample is pipetted into a 400-ml beaker and diluted with water to about 200 ml. A solution of 1N silver nitrate is added until a few drops of the reagent cease to cause cloudiness when added to the clear portion of the solution after the silver chloride has been allowed to settle. A few drops of methyl orange are added, followed by a saturated solution of sodium carbonate until the neutral point of methyl orange is reached. With 6N H_2SO_4 added the solution is made just acid to methyl orange, and then a large excess of 10 per cent

zinc oxide emulsion is added. The solution is filtered by suction through a fine sintered-glass funnel, and the precipitate is washed with small portions of water (the suction is released and the solution stirred well after each addition of water). To the filtrate is added 10 ml of sulfuric acid per 100 ml of filtrate, and the solution is cooled to 10 to 20°C. Next, 2 to 3 g of sodium bismuthate is added to the solution, which is stirred for 5 min and then filtered through a sintered-glass filter. The precipitate is washed with 3 per cent sulfuric acid until the washings are colorless. Two drops of 1,10-phenanthroline indicator are added to the solution, which is immediately titrated with 0.1N ferrous sulfate to the appearance of the permanent pink color.

If an appreciable amount of cobalt is present in the sample, 20 ml of glacial acetic acid and 10 g of ammonium acetate are added to the filtered solution after the zinc oxide precipitation. The filtrate is heated to about 80°C and gassed with H_2S for about 15 min. It is then filtered through a Whatman No. 40 (or similar) filter paper, and the filtrate is tested with a little more H_2S to ensure that precipitation is complete. The solution is then boiled for a few minutes to get rid of the H_2S , and the procedure is continued as above. The additional step removes the cobalt, which would otherwise cause high results.

If organic material is present, as would be indicated by a brownish color in the filtrate, it is necessary to add 1 g more of sodium bismuthate to the filtrate and boil it for several minutes. The pink permanganate color should persist. If it disappears, it is necessary to add more bismuthate until it does persist. The sample is then cooled to 10 to 20°C and titrated as above.

(3) Uranium Metal. The following semimicro method has been used for the determination of manganese in uranium metal:

Procedure.⁶ A 5- to 6-g sample is taken, cleaned with dilute HNO_3 (1 to 2), dried, and accurately weighed. The sample is dissolved in 30 ml of acid mixture (8 g of $AgNO_3$ is dissolved in 525 ml of cold water; 100 ml of H_2SO_4 is carefully added while stirring; the solution is cooled, and then 125 ml of 85 per cent H_3PO_4 and 250 ml of HNO_3 are added while stirring) in a 400-ml beaker at a low temperature. When solution is complete, 50 ml of water is added and the solution is boiled vigorously for 1 to 2 min. It is then cooled somewhat, and 50 to 60 ml of H_2O and 0.6 to 0.7 g of $(NH_4)_2S_2O_8$ are added. When the salt has dissolved, the solution is brought to a boil and is boiled vigorously for 1 to 2 min. It is next cooled to 15 to 20°C in cold running water; when cool, it is diluted with 100 to 125 ml of ice water. Finally the solution is titrated potentiometrically with sodium arsenite solution (1 ml equals 0.000115 g of Mn), using a Beckman pH meter or the equivalent.

(b) Colorimetric Methods. Micro amounts of manganese are usually determined by colorimetric methods after the manganese has been oxidized to the permanganate ion.⁷⁻¹⁰

The periodate oxidation in nitric acid solution has been used to the greatest extent. The use of persulfate requires the presence of the catalyst AgNO_3 . The maximum light absorption of the permanganate

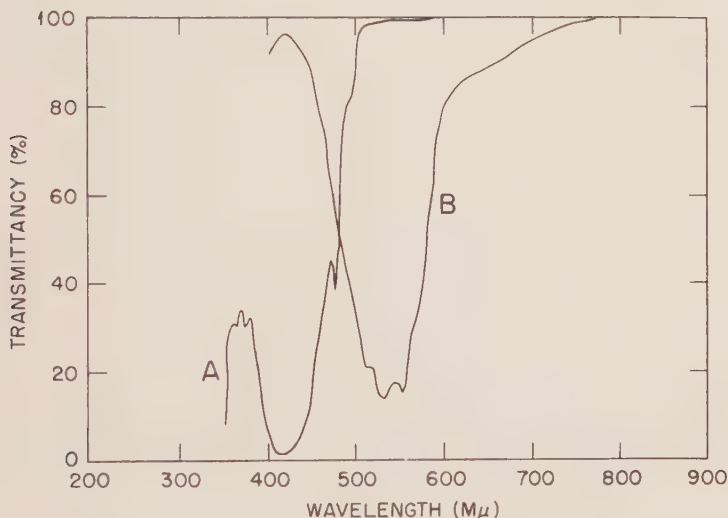


Fig. 17.1—Spectral transmittancy curves. Curve A, uranyl nitrate (nitric acid solution containing 2.36 g of uranium per 100 ml). Curve B, permanganate [solution containing 500 γ of manganese per 50 ml of HNO_3 (1 to 1), and oxidized with periodate]. Measurement made with a Beckman spectrophotometer (2-cm cells, 2-m μ band width).

occurs at 525 m μ . In this region the absorption due to uranium is negligible if a spectrophotometer transmitting a band width of 5 m μ or less is used. With wider band widths the effect of the uranium (Fig. 17.1) is appreciable, and the transmittancy must be measured against a solution containing the same amount of uranium, but no manganese.

Procedure.¹⁰ A 5.90-g sample of the oxidized metal is weighed out and transferred to a 150-ml beaker. Fifty milliliters of dilute HNO_3 (1 to 1) is added, the beaker is covered, and the sample is boiled until it is in solution. Then 0.5 g of potassium periodate is added, and the solution is boiled for at least 5 min to ensure the complete oxidation of the manganese. The solution is cooled, diluted to 50 ml, and centrifuged. The transmittancy of the solution is measured against distilled

water at 525 $m\mu$ with a spectrophotometer transmitting a band width of 5 $m\mu$ or less.

A transmittancy-concentration curve is prepared by taking 25, 50, 100, 200, 300, and 500 γ , successively, of manganese in the presence of 5.9 g of U_3O_8 and carrying the samples through the procedure. The transmittancy is plotted against the concentration on semilog paper.

The procedure described may be used for uranium metal. The range is 0.5 to 10.0 γ of manganese per milliliter, with an accuracy depending upon the range but of the order of 5 to 10 per cent. By decreasing the volume and increasing the length of the cells (see Chap. 24, "Photometric Methods") the sensitivity is greatly increased.⁹ The useful range is from 0.75 to 10 γ of manganese, 1 ml being used for the final volume. The accuracy is likewise of the order of 5 to 10 per cent.

Spectrographic methods were used for the determination of manganese in uranium-bearing material¹¹ as well as in lime, aluminum, calcium, magnesium, and other metals.^{12,13}

2. TECHNETIUM

A counting method for the determination of radioactive technetium, utilizing the distillation of the oxide from perchloric acid solution into sodium hydroxide followed by the precipitation of the radioactive technetium with Re_2S_7 as a carrier, has found application.¹⁴

3. RHENIUM

The determination of rhenium was not necessary for routine control. Harrison¹⁵ has been able to determine 25 ppm in uranium-base materials by spectrographic means. A colorimetric method based on the extraction of the thiocyanate complex by amyl alcohol¹⁶ was used by Williams¹⁷ for uranium-base materials.

Procedure.¹⁷ A 50-g sample is weighed into a 250-ml beaker and dissolved in nitric acid. The solution is evaporated to the stage at which crystallization begins, 75 ml of HCl is added, and the evaporation is repeated. The HCl evaporation is repeated three times in order to remove nitric acid. The beaker is removed from the source of heat, and 100 ml of water is added. The solution is stirred, cooled, and transferred to a 250-ml separatory funnel. Six milliliters of 20 per cent potassium thiocyanate solution is added, and the funnel is shaken; then 2 ml of 25 per cent stannous chloride (in 6N HCl) solution is added, and the funnel is shaken again. If the sample contains much copper, a precipitate of $CuCNS$ will form at this stage, and it may be necessary to increase the quantities of potassium thiocyanate

and stannous chloride. Now 15 ml of amyl alcohol is added, and the solution is shaken vigorously. The aqueous layer is withdrawn, and the amyl alcohol extract is transferred to a 150-ml beaker. The extractions on the aqueous layer are repeated a second and a third time, using 10-ml quantities of amyl alcohol and adding the extracts to the 150-ml beaker (if a precipitate forms at the water-amyl alcohol interface, it is necessary to filter the combined amyl alcohol extracts through glass wool into another 150-ml beaker). The aqueous layer is discarded, and the combined amyl alcohol extracts are transferred to a 100-ml separatory funnel. The solution is shaken three times with 5 ml of dilute HCl (1 to 4), and the aqueous layer is discarded in order to remove most of the uranyl and stannous chlorides dissolved in the amyl alcohol. The amyl alcohol solution is transferred to a 150-ml beaker and evaporated carefully to a volume of about 2 ml, which is then allowed to cool; about 1 ml of HNO_3 is then cautiously added. After the initial vigorous reaction has subsided, another 5 ml of HNO_3 is added, the solution is gently heated in order to complete the oxidation, 30 ml of HCl is added, and the solution is then evaporated to 2 ml. This process is repeated three times in order to remove HNO_3 . The solution is then diluted with 50 ml of water and cooled, and 2 g of cupferron in 10 ml of water is added. The solution is swirled, allowed to stand for a few minutes (sufficient cupferron should be added to precipitate completely any Mo, W, or Sn present), and then filtered into a 150-ml beaker, the precipitate being allowed to drain. The filtrate (which may be slightly cloudy) is transferred to a 100-ml separatory funnel and is extracted with three successive 20-ml portions of chloroform. Ten milliliters of HCl is added, the solution is extracted twice with 20-ml portions of chloroform, and the chloroform extracts are discarded. Six milliliters of potassium thiocyanate solution and 2 ml of stannous chloride solution are added to the aqueous layer, which is then shaken and extracted with 8 ml of amyl alcohol. The amyl alcohol extract, containing any rhenium as thiocyanate, is diluted to 10 ml, and the entrained water is removed by centrifuging. The orange-yellow color of the amyl alcohol is measured with a Spekker absorptiometer by using a 1-cm cell and No. 6 light-blue filters. The amount of rhenium is determined from a previously prepared graph.

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Chapter 18

CHROMIUM, MOLYBDENUM, AND TUNGSTEN

By K. J. Jensen and Boyd Weaver

Analytical methods were necessary for chromium, molybdenum, and tungsten under a wide variety of conditions and at different concentrations.

1. CHROMIUM

1.1 Methods of Solution. Uranium metal, U_3O_8 , and UO_2 were dissolved in nitric acid. With some residues standard methods¹ of decomposition were used. The material was broken up by a potassium pyrosulfate fusion, followed by an acid leach. Any residue from this leach was fused with a mixture of sodium carbonate and potassium chlorate.

Chromium-uranium alloys were quickly dissolved by treating with HCl (1 to 1), heating, and, after most of the sample had disintegrated, adding hydrogen peroxide to complete the solution of uranium.

1.2 Methods of Determination. (a) Volumetric Methods. The most widely used method for determining macro amounts of chromium has been the reduction of chromium(VI) with standard ferrous sulfate solution.² With various modifications this method has been used for numerous types of samples, including many that contain uranium.³⁻⁷ In the course of the procedure chromic ion is oxidized to the hexavalent state in an acid medium by ammonium persulfate in the presence of silver ion. The chromium is estimated by adding an excess of standard ferrous sulfate solution and back-titrating with standard permanganate or ceric sulfate solution, using ferrous phenanthroline complex, ferroin, as an indicator. This procedure is subject to few interferences. However, any substance that is reduced by the ferrous sulfate solution and not reoxidized rapidly by the ceric sulfate will

interfere with the analysis. One interference of this type, manganese, for example, can be eliminated by the addition of a reducing agent, such as sodium azide or dilute hydrochloric acid, which preferentially reduces the permanganate. After the excess persulfate has been destroyed, sodium azide or dilute hydrochloric acid is added, and the solution is boiled for a short time.

Vanadium is a disturbing element since it is oxidized to the vanadate state (VO_3^-) by the persulfate and reduced to the vanadyl state (VO^{++}) by the ferrous sulfate. The vanadyl ion is slowly reoxidized to the vanadate state by the ceric sulfate, a constantly fading end point being produced. Although the titration to a permanent end point is possible, large amounts of vanadium should be separated from the chromium. This separation can be accomplished by precipitating vanadium cupferrate from a strongly acid solution⁸ with a pH between 1.2 and 1.6. In the procedures involving titration with permanganate, vanadium does not interfere.⁹

Procedure.⁵ The sample is dissolved in 25 to 50 ml of hydrochloric acid, heated, and finally cleared by adding 5 to 10 ml of 30 per cent hydrogen peroxide and heating for a few more minutes. Ten to fifteen milliliters of sulfuric acid is added, and the solution is evaporated slowly until strong fumes of sulfuric trioxide are evolved. The solution is cooled and diluted carefully with 200 to 250 ml of water. Between 0.05 and 0.1 g of silver nitrate and 3 to 5 g of ammonium persulfate are then added, and the solution is boiled vigorously for 10 to 20 min. The solution is then cooled, a measured volume of freshly standardized ferrous sulfate is added, and the unoxidized excess is back-titrated with standard ceric sulfate solution, using 1 or 2 drops of ferroin as an indicator.

A semimicro method⁶ for small amounts of chromium in process solutions follows a modification of the usual procedure. When manganese is absent, a small amount of a manganous salt is added. The permanganate formed acts as an indicator of the completeness of the oxidation. The excess permanganate is then reduced by boiling with dilute hydrochloric acid. Phosphoric acid is added to complex the ferric iron and eliminate its color. A measured volume of standard ferrous sulfate solution is added from a microburet, and the excess is back-titrated with standard ceric sulfate solution from a microburet. When the end point has been just reached, but not exceeded, an amount of ferrous sulfate solution exactly equal to the quantity previously used is added and titrated with the ceric sulfate. Thus the standardization and sample titration are made under similar conditions. With this procedure amounts of chromium from 2.5 to 25 mg may be determined with an accuracy of ± 2 per cent.

(b) Colorimetric Methods. (1) Diphenylcarbazide Method. The production of an intense color by chromate ion with *s*-diphenylcarbazide was first observed¹⁰ in 1900, and it has been the subject of many investigations¹¹⁻¹³ since that time. This very sensitive and selective reagent has been used for the determination of small amounts of chromium in uranium materials and process solutions. Much work has been done in adapting this reagent to special needs.¹⁴⁻²⁰ Interferences have been studied, and special absorption cells have been devised which have increased the range of the method. Two procedures will be described, one for general use with solutions not containing much uranium and one for micro amounts of chromium in uranium metal and ores.

Chromium is oxidized to the hexavalent state and made slightly acid with acetic or sulfuric acid, and a solution of *s*-diphenylcarbazide is added. The hexavalent chromium reacts with the diphenylcarbazide to form a soluble reddish-purple complex of unknown composition. The absorption of light by the solution is at a maximum at approximately 540 m μ . Beer's law is obeyed.

The only other element giving a violet color is molybdenum(VI), but the color is much less intense.¹³ Molybdenum(VI) can be quantitatively separated by extraction with ethyl or isopropyl ether from a hydrochloric acid solution. Mercury(I) and mercury(II) produce pale blue colors, which can be entirely eliminated by chloride ions.¹⁸

Iron and vanadium interfere because of the formation of yellow or yellow-brown complexes with the reagent. However, their absorption at 540 m μ is not high. (As much as 100 γ of iron may be present in the final solution without serious interference, but larger amounts should be removed.) Iron(III) is precipitated as the hydrous oxide during the procedure, and as much as 500 γ of iron has been removed in this manner with satisfactory results. The color of the vanadium diphenylcarbazide complex fades more rapidly than the color of the chromate; it has been found¹³ to be negligible after 15 min if the ratio of vanadium to chromium is less than 10 to 1. Vanadate can be extracted with chloroform as the 8-hydroxyquinolate, or it can be separated by precipitation or extraction as the cupferrate.

Bismuth interferes in the presence of phosphate through coprecipitation of chromium in a neutral or basic solution. The bismuth phosphate may be removed in a slightly acid solution without coprecipitation of the chromium. The effects of the other ions are summarized in Table 18.1. The maximum amounts of interfering elements permissible for 5 per cent accuracy are given.

Most of the metal ions tested give precipitates in the basic medium used for the oxidation step and can be removed by filtration if they

are present after acidification. The interference by manganese can be removed by treatment with sodium azide or chloride, as described above in the volumetric procedure.

With 25-ml volumes and a Coleman model 10S spectrophotometer the range of the method is 1 to 14 γ of chromium. Special cuvettes

Table 18.1—Interference by Various Ions in the Determination of Chromium by the Diphenylcarbazine Method

Ion added	Amount added, γ	Chromium present, γ	Chromium found, γ	Recovery, %	Amount permissible, γ
Al ⁺ ³	100	4.0	4.1	103	100
Bi ⁺ ³	1,000	4.0	3.9	98	1,000*
Ce ⁺ ⁴	1,000	4.0	4.0	100	1,000*
HCOO ⁻	1,000	4.0	4.1	103	1,000*
C ₂ O ₄ ⁻ ⁻	1,000	4.0	4.1	103	1,000*
Cu ⁺ ⁺⁺	1,000	4.0	4.1	103	100
F ⁻	1,000	4.0	3.6	90	500
Fe ⁺ ³	500	4.0	3.9	98	500*
Hg ⁺ ⁺⁺	1,000	4.0	4.0	100	1,000
Mn ⁺ ⁺⁺	5	4.0	4.1	103	5
Mo ⁺ ⁶	100	4.0	4.1	103	100
Ni ⁺ ⁺⁺	100	4.0	4.2	105	100
PO ₄ ⁻ ³	1,000	4.0	3.6	90	500
SiO ₃ ⁻ ⁻	1,000	4.0	4.0	100	1,000*
Sn ⁺ ⁺⁺	1,000	4.0	4.0	100	1,000*
UO ₂ ⁺ ⁺⁺	3,000	4.0	3.8	95	3,000*
Zn ⁺ ⁺⁺	100	4.0	4.0	100	100
Zr ⁺ ⁴	1,000	4.0	4.4	110	500
NO ₃ ⁻	10,000	0.30	0.3	100	10,000

*This is the largest amount added; larger amounts may not interfere.

have been designed for use with the Beckman spectrophotometer, and these can lower the range to 0.01 to 0.20 γ of chromium (see Chap. 24, "Photometric Methods"). The results are accurate within 5 per cent.

Procedure for Solutions.¹⁶ A suitable aliquot, dissolved preferably in sulfuric acid, is placed in a 50-ml beaker and is made just alkaline with 5 per cent sodium hydroxide. Seven drops more of sodium hydroxide and 5 drops of bromine are added, and the solution is heated gently until the yellow color of the bromine disappears. After cooling, 0.5 ml of glacial acetic acid is added, any precipitate present is removed by filtration, and the solution is transferred to a 25-ml volumetric flask. Three drops of 5 per cent phenol solution are added to

remove the last trace of bromine, and the solution is cooled in an ice bath. One milliliter of the diphenylcarbazide solution (50 mg of diphenylcarbazide in 3 ml of glacial acetic acid, diluted to 25 ml with ethanol) is added, the solution is diluted to volume, and the transmittancy is measured at $540\text{ m}\mu$ against distilled water. Since the development of the color depends on the temperature and time of standing and is not permanent, it is well to take readings at 5-min intervals until a maximum is reached. Ten to fifteen minutes is usually sufficient. A blank correction is determined by carrying the reagents through the same procedure. The amount of chromium present is determined from a previously prepared transmittancy-concentration curve.

The above procedure, although useful for the analysis of samples containing not too many interfering substances, is not applicable for the determination of small amounts of chromium in uranium metal or oxide because excessive amounts of sodium uranate precipitate in the basic medium used for the oxidation.

Other reagents, including permanganate, have also been used to effect the oxidation. Potassium permanganate offers an advantage over the bromine method in the determination of chromium in uranium metal and oxides in that the oxidation is performed in an acid medium and no precipitate of sodium uranate is formed.

Procedure for Uranium Metal and Oxides.¹⁵ About 1 g of metal or metal oxide is dissolved in nitric acid. After solution is complete, 12.5 ml of 10 per cent sulfuric acid is added, and the solution is evaporated to fumes of sulfur trioxide. A little water and a few drops of ethanol are added, and the solution is evaporated again to fumes. The ethanol reduces any chromate that may have been formed by the nitric acid treatment. The evaporated solution is diluted to 25 ml in a volumetric flask. Two 10-ml aliquots of this solution are taken; one is placed in a 25-ml volumetric flask, the other in a small beaker. To the aliquot in the beaker a sufficient amount (usually 4 to 6 drops) of 0.1N potassium permanganate is added to give the solution a distinct pink color. This solution is boiled for 2 min, sodium azide is added in small quantities until the pink color is completely discharged, and the excess hydrazoic acid is removed by boiling for another minute. The solution is then allowed to cool and is transferred to a 25-ml volumetric flask. One milliliter of diphenylcarbazide solution (1 per cent in ethanol) is added to each of the two aliquots, which are then diluted to volume. The transmittancy of the solution that had the permanganate treatment is measured against that of the solution to which only the reagent was added. From a calibration curve made with known amounts of chromium in the presence of uranium, the amount of chromium in the aliquot can be obtained.

(2) Chromate-Ferric Perchlorate Method. The ferric perchlorate method, by which the chromate color is intensified about five times, was developed for the analysis of stainless steel.²¹ An investigation²² was made of an application of this method to material of which uranium is a major constituent. The procedure adopted differs slightly from the original. It was found useful for the range of 0.1 to 1.0 mg of chromium.

Procedure.²² To a solid sample of suitable size in a 150-ml beaker 2 ml of hydrochloric acid and 10 ml of nitric acid are added. The solution is heated until the evolution of brown fumes ceases. Two successive 5-ml portions of nitric acid are then added, and the solution is evaporated to 5 ml. Any remaining brown, or green, insoluble material is dissolved by careful fuming with 5 ml of 70 per cent perchloric acid under a cover glass. Any white insoluble material remaining is filtered off after dilution to 15 ml with water. To the solution are added 7.23 g of ferric nitrate crystals and 20 ml of 70 per cent perchloric acid. The beaker is covered and heated until white fumes are evolved and the solution begins to thicken and bubble. The solution is cooled, and the condensate is washed from the cover glass into the beaker. The crystals are dissolved in water, and the solution is transferred to a 50-ml volumetric flask and diluted to the mark. A portion is transferred to a 1-cm absorption cell, and the optical density at 410 $m\mu$ is measured against water. To the remainder of the solution in the flask a few crystals of ferrous sulfate are added and mixed until the intense yellow color disappears. The optical density of this solution is then measured against water. From the two optical densities the amount of chromium in the sample can be calculated by means of previously prepared calibration curves.

2. MOLYBDENUM

2.1 Methods of Solution. Molybdenum metal can be dissolved by a variety of solvents. It is soluble in aqua regia, sulfuric acid, and dilute nitric acid. A mixture of sodium carbonate and potassium nitrate can be used to fuse the metal and produce a soluble molybdate. Hydrochloric acid, hydrofluoric acid, and dilute sulfuric acid are ineffective in dissolving molybdenum. Oxidizing agents, however, such as hydrogen peroxide and ammonium persulfate, convert the black residue left after treatment with hydrochloric acid or dilute sulfuric acid into soluble molybdic acid. Uranium-molybdenum alloys (less than 20 per cent molybdenum) can be dissolved by treatment with hydrochloric acid, followed by the addition of small amounts of nitric acid. The only satisfactory solvent for those alloys that are higher in molybdenum is nitric acid or nitric-hydrochloric acid mixtures.

Sometimes it is necessary to filter and ignite the small amount of residue remaining and to dissolve this material with smaller amounts of the acids.

Many uranium-molybdenum alloys have been analyzed for molybdenum by precipitating the molybdenum as lead molybdate from a faintly acidic acetate solution. This procedure has been found effective in separating molybdenum from uranium in alloys containing molybdenum in amounts as low as 1 per cent.

A few separations based on the solubility of certain molybdenum compounds in organic solvents are available. Molybdenum in a hydrochloric acid solution containing some ferric iron is extracted by diethyl ether in the cold. Other elements, especially the trichlorides of iron, gold, and thallium, and, to a lesser extent, antimony, arsenic, tellurium, germanium, and tin, are also extracted.³⁹ In the colorimetric determination of molybdenum, the thiocyanate complex of quinquevalent molybdenum is extracted from most interferences with solvents such as diethyl ether, butyl acetate, or hexanol. Chloroform has been used to extract small amounts of the α -benzoinoxime complex. Molybdenum(VI) cupferrate is extracted with chloroform in acid medium.

When dry hydrogen chloride is passed over molybdic oxide at slightly elevated temperatures, a volatile compound, which may be represented as $\text{MoO}_3 \cdot 2\text{HCl}$, is formed. The volatilization of this compound has been found² to begin at 200°C and to be complete at 290°C . The volatility of $\text{MoO}_3 \cdot 2\text{HCl}$ has been used as a method of separating molybdenum from uranium.²³

A possibility for the separation of many metals from molybdenum arises from the fact that molybdenum, when present in a slightly acid and nearly uranium-free solution, is electrolytically deposited in a mercury cathode, but when much uranium is present, no molybdenum is deposited. This effect has been verified²⁴ for amounts of molybdenum from 0.1 to 1.0 mg in the presence of 10 g of uranyl sulfate. A mercury-cathode electrolysis apparatus with a small anode (1 cm of platinum wire of approximately 1.5 mm diameter), operating with a current of about 0.9 amp and a potential of 10 volts, was used.

When a uranium-molybdenum solution is treated with ammonium hydroxide, the uranium precipitate retains some of the molybdenum.²⁵ Moreover, the molybdenum may prevent the complete precipitation of the uranium; it is not volatilized quantitatively as molybdic oxide when ammonium diuranate is ignited to oxide.

To a series of samples containing an amount of uranyl chloride equivalent to 0.4750 g of U_3O_8 , varying amounts of molybdenum were added as ammonium molybdate. The volumes were adjusted to 100 ml,

and the uranium was precipitated by adding 6N ammonium hydroxide until the phenolphthalein end point was reached. The precipitates were filtered off and ignited for varying periods and at varying temperatures. The results obtained are given in Table 18.2.²⁵

2.2 Methods of Determination. Macro amounts of molybdenum can be determined both by gravimetric and by volumetric methods.

Table 18.2—Effect of the Presence of Molybdenum on the Precipitation of Uranium as $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and Its Ignition to U_3O_8

U/Mo weight ratio	Ignition conditions	Weight of ignited product, g
40/1	(a): 1 hr at 850°C	0.4775
	(b): (a) + overnight at 1050°C	0.4750
	(c): (b) + 1½ hr at 1250°C	0.4771
	(d): (c) + 2 hr at 850°C	0.4742
10/1	(a) above	0.4997
	(b) above	0.4965
	(c) above	0.4935
2/1	(a) above	0.5615
	(b) above	0.5586
	(c) above	0.5567
1/1	(a) above	0.5878
	(b) above	0.5846
	(c) above	0.5567
1/10	(a) above	0.5960
	(b) above	0.5920
	(c) above	0.5806
1/50	(a) above	0.4190
	(b) above	0.4162
	(c) above	0.4080

The gravimetric methods commonly used include the precipitation of the molybdenum as lead molybdate, molybdenum sulfide,²⁶ or the molybdenum complex of α -benzoinoxime.²⁷ The lead molybdate precipitate is ignited and weighed as such, but molybdenum sulfide or the molybdenum complex with α -benzoinoxime is ignited to the oxide and weighed.

The volumetric determination of molybdenum, after its separation as volatile $\text{MoO}_3 \cdot 2\text{HCl}$ or insoluble thorium molybdate and subsequent reduction in a Jones reductor, has been employed.^{23, 28} The simultaneous titration of uranium and molybdenum was found to be unreliable.

Colorimetric methods based on the colored compounds formed by molybdenum in the presence of thiocyanate and phenylhydrazine²⁹ have been used.^{24, 30-35}

(a) Volumetric Methods. (1) Thorium Molybdate-Ceric Sulfate Method.²⁸ Some workers have employed a volumetric method for the determination of molybdenum in uranium-molybdenum alloys whereby molybdenum is precipitated as thorium molybdate, thus separating it from uranium. The precipitate is then dissolved, and the molybdenum is determined volumetrically by the procedure described below.

The solution of molybdenum is passed through a Jones reductor and caught in an excess of ferric ammonium sulfate. The ferrous ion formed is titrated with ceric sulfate solution.

Substances forming reduced compounds that can be oxidized by the titrant must be absent. These include iron, uranium, chromium, vanadium, titanium, columbium, arsenic, tungsten, antimony, nitric acid, organic matter, and polythionic acids. Of these interferences, uranium is the only one present in the alloys, and it can be removed by the procedure described below.

Using 0.1N ceric sulfate solution, 35 to 160 mg of molybdenum can be conveniently handled. The method is accurate to ± 0.3 per cent.

Procedure.²⁸ To a 5-g sample about 50 ml of HCl (1 to 1) is added. If no reaction occurs, the solution is warmed. Hydrogen peroxide (30 per cent) is added to dissolve the black hydrated uranium dioxide and to oxidize both elements to the hexavalent state. The solution is boiled for about 10 min to destroy the excess of peroxide; it is then cooled and diluted to 1 liter.

In the event that the HCl (1 to 1) does not dissolve the sample, a little HNO_3 is added and the solution is boiled. After it has dissolved completely and cooled, it is diluted to 1 liter, as above. (It is best to avoid the use of HNO_3 , if possible, for it must be removed before reducing in the Jones reductor and titrating the uranium. The HNO_3 cannot be fumed off directly after dissolving, because the use of sulfuric acid later precipitates thorium sulfate and because fuming with perchloric acid causes MoO_3 to precipitate.)

Half-gram samples (instead of the larger samples) may be dissolved as above if the only available quantities of the alloy are small or if heterogeneity is to be revealed.

A 100-ml aliquot of the liter of solution is titrated roughly with dilute ammonium hydroxide to determine its acidity. To another aliquot is added 16 ml of glacial acetic acid, followed by the volume of ammonium hydroxide required to neutralize the HCl. It is important to add the acetic acid first in order to prevent the formation of a precipitate that is very slowly soluble in acetic acid. The solution is diluted to about 200 ml.

If a small sample of alloy is dissolved, enough ammonium acetate is added to react with the mineral acid present. The solution is then

diluted to about 200 ml. In either case the solution should be about 7 per cent in acetic acid.

About 25 ml of thick paper pulp is added, and the molybdenum is precipitated as $\text{Th}(\text{MoO}_4)_2$ with a thorium perchlorate solution (1 ml is equivalent to about 5 mg of Mo). The thorium perchlorate is added from a buret slowly with stirring until a 50 per cent excess is present. The contents of the beaker are digested just below the boiling point for about 15 min. The thorium molybdate is filtered, while hot, with a Whatman No. 42 filter paper and is washed well with hot dilute acetic acid.

The filter and the $\text{Th}(\text{MoO}_4)_2$ are transferred back to the original 400-ml beaker. Twenty-five milliliters of concentrated HCl is added to each beaker, and the contents are stirred until the filter paper has disintegrated. Then 75 ml of water is added to each beaker, and the thorium molybdate-filter pulp-HCl mixture is heated nearly to boiling for about 15 min.

The thorium solution, containing the filter pulp, is filtered through an 11-cm Whatman No. 42 filter paper, and the filter is washed several times with boiling HCl (1 to 25). After cooling, the filtrate is passed through a Jones reductor into an excess of ferric alum. The ferrous iron, equivalent to the molybdenum, is then titrated with ceric sulfate, using ferroin as the indicator.

(b) Colorimetric Methods. (1) Standard Thiocyanate Method. A method was needed for determining micro amounts of molybdenum in uranium metal and various uranium compounds. The well-known molybdenum thiocyanate method²⁹ has been adapted for use in uranium samples. Many variations of essentially the same method have been used by the Project's various analytical laboratories (see references 30-32, 34, 35).

The following procedure has been used for hundreds of uranium-metal samples. The molybdenum thiocyanate complex in a sulfuric acid solution is extracted with butyl acetate, some uranium accompanying the molybdenum. Washing the butyl acetate extract with H_2SO_4 (1 to 9) removes practically all the uranium. The transmittancy of the solution is then measured at 470 $\text{m}\mu$. The range is 5 to 50 γ with a final volume of 25 ml of solution.

Procedure.³⁴ Uranium metal and oxides can readily be converted to uranium trioxide, and uranium tetrafluoride to uranyl sulfate. The sample is taken up in 20 ml of H_2SO_4 (1 to 1), diluted to 75 ml, and cooled to 10 to 15°C. All the reagents are cooled. Two milliliters of 20 per cent NH_4CNS solution is added, and the solution is shaken. Then 5 ml of SnCl_2 solution [prepared by heating on a steam bath 350 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 200 ml of HCl (1 to 1) until solution occurs, allowing to stand overnight, filtering, and then diluting to 1 liter with

freshly boiled water] is added. The solution is extracted with 25 ml of butyl acetate. The butyl acetate layer is separated and washed with a mixture of 50 ml of H_2SO_4 (1 to 9), 2 ml of 20 per cent NH_4CNS , and 2 ml of SnCl_2 solution. The transmittancy is measured with a Beckman spectrophotometer (2-cm cells) at 470 $\text{m}\mu$ against a blank containing approximately the same amount of molybdenum-free uranium, which is carried through the procedure.

A transmittancy-concentration curve is prepared by taking 10, 20, 30, 40, and 50 γ of molybdenum in the presence of 0.5 g of uranium and carrying the solutions through the procedure.

(2) Phenylhydrazine Method. A method based on the colored complex of molybdenum with phenylhydrazine³⁸ has been investigated³³ and applied to solutions containing relatively large amounts of U, Fe, Cr, Ni, Cu, Mn, and W. Since the red color with phenylhydrazine is specific with molybdenum, no separations need be made from other elements except when they have colors sufficiently strong to interfere. When interfering metals are present in large amounts relative to the molybdenum, they may be removed by simple separation procedures. Uranium is best precipitated as the peroxide, and the other metals as hydroxides.

Procedure.³³ Uranium is removed as the peroxide by precipitation with hydrogen peroxide at a pH of 1.3 and at a low temperature. The precipitate is filtered off on a fine glass filter, and the excess peroxide is removed from the filtrate by boiling. Sufficient ferrous sulfate is added to reduce all the chromate. Sodium hydroxide is added in slight excess, and the solution is boiled until all the ammonia has been removed and the hydroxides have precipitated. The precipitate is removed by filtration on a fine paper or glass filter. The filtrate is slightly acidified with sulfuric acid and evaporated to 10 ml if the sample contains less than 100 γ of molybdenum, or it is diluted in a volumetric flask if an aliquot is to be taken.

Between 10 and 20 ml of solution is placed in a 50-ml Nessler tube. A volume of standard molybdate solution containing within 25 per cent of the amount of molybdenum expected in the sample is placed in another tube, and the solution is diluted to the volume of the sample solution. Five milliliters of 3 per cent phenylhydrazine in 1N sulfuric acid is added to each tube and mixed. The tubes are left in a water bath at 80°C for 15 min and cooled for 30 min. They are then filtered through fine paper into colorimetric comparison cells.

3. TUNGSTEN

3.1 Methods of Solution. Uranium-tungsten alloys were found to dissolve readily when treated first with nitric acid and then with a

few milliliters of hydrofluoric acid.³⁷ This procedure leaves the tungsten in solution as the complex ion $\text{WO}_2\text{F}_4^{--}$.

3.2 Methods of Separation. Tungsten is precipitated quantitatively by α -benzoinoxime.²⁷ In one method³⁰ use is made of this fact in the micro determination of tungsten. Molybdenum and tungsten are co-precipitated with α -benzoinoxime, ignited, and fused with a flux. The melt is dissolved in water and made acid with sulfuric acid. A reducing agent (thioglycolic acid) and potassium thiocyanate are added. The resulting colored molybdenum complex is extracted with butyl acetate, and the tungsten is determined in the remaining aqueous solution.

3.3 Methods of Determination. (a) Gravimetric Methods. Tungsten is customarily precipitated as tungstic oxide and weighed as such. For tungsten in uranium alloys some workers determined the tungsten by dehydrating the solution with perchloric acid, filtering, and weighing the ignited precipitate.³⁷ If chromate, molybdate, and sulfate ions are absent, tungsten may be precipitated as mercurous tungstate, ignited, and weighed as tungstic oxide.

(b) Colorimetric Method. (1) Dithiol Method. The blue color of the tungsten complex with toluene-3,4-dithiol has been applied to the determination of traces of tungsten in uranium materials.^{30,38} This method requires a preliminary separation with α -benzoinoxime, followed by removal of the molybdenum.

Procedure.³⁰ Five milliliters of sulfuric acid is added to a sample of suitable size, and the solution is heated to fumes of sulfur trioxide, then cooled, and diluted to 100 ml. Fifteen milliliters of α -benzoinoxime solution (2 g in 100 ml of ethanol) is added with stirring, followed by enough bromine water to color the solution yellow and by another 10 ml of α -benzoinoxime solution. The solution is allowed to stand for 20 min at a temperature of 10°C. A little filter-paper pulp is stirred in, and the solution is filtered through a Whatman No. 40 filter paper. The precipitate is washed with dilute sulfuric acid containing a little reagent and finally with water. The paper and precipitate are ignited at the lowest possible temperature. The residue is fused with a small amount of fusion mixture (1 part of Na_2CO_3 to 2 parts of K_2CO_3) and leached with water. Any insoluble material is filtered off.

The molybdenum is separated by extraction as follows: Six drops of 50 per cent thioglycolic acid are added, followed by 1 ml of 20 per cent potassium thiocyanate solution. Seven milliliters of sulfuric acid is added for each 30 ml of solution. The solution is cooled for 15 min, and the molybdenum is extracted as the thiocyanate complex with butyl acetate. Tungsten is then determined in the aqueous layer.

Nitric acid is added to the aqueous layer, and the solution is heated to fumes of sulfur trioxide. After cooling, the sides of the beaker are rinsed with water, and the solution is again evaporated to fumes of sulfur trioxide to remove the last traces of nitric acid. The solution is cooled, diluted, and made just ammoniacal. Half a milliliter of dithiol solution (0.2 per cent in 1 per cent NaOH) is added, followed by 5N sulfuric acid until a distinct turbidity appears. An excess of 5 drops of acid is added, and the solution is allowed to stand for 20 min. The tungsten complex is extracted with small amounts of chloroform, which are then filtered through dry paper into a measuring cylinder. The volume is adjusted with butyl acetate to the desired amount, and the optical density is measured with a Spekker colorimeter, using a red filter. The amount of tungsten is determined from a previously prepared curve.

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Chapter 19

VANADIUM, COLUMBIUM, AND TANTALUM

By S. W. Rasmussen and C. J. Rodden

Vanadium has been of interest because of its occurrence in uranium-bearing ores. Methods for the determination of trace amounts of columbium and tantalum have also been developed.

1. VANADIUM

The quantity of vanadium in minerals and in uranium concentrates varies from a trace to the proportions of a major constituent.

Macro amounts of vanadium are generally determined by oxidation or reduction reactions involving a change of valence from +4 to +5, or the reverse. For micro amounts colorimetric methods are usually employed. These methods may use cupferron,¹ peroxide,^{2,16} oxine,^{3,16} or phosphotungstic acid.^{16,29} Spectrographic methods have been used at several sites⁴⁻⁶ for the determination of small amounts.

1.1 Solution of Samples. Vanadium salts are soluble in strong acids. Vanadium in uranium metal and oxides gives soluble vanadic acid when treated with nitric acid. A mixture of sulfuric and hydrofluoric acids usually gives a soluble vanadate with vanadium in ash and similar material. A mixture of sulfuric, nitric, perchloric, and hydrofluoric acids dissolves vanadium from carnotite-bearing sandstone. For more complex minerals fusion with sodium carbonate and sodium nitrate or sodium peroxide is usually sufficient.⁷

1.2 Methods of Separation. Macro quantities of vanadium are usually determined volumetrically in the original sample even in the presence of chromium, manganese, iron, titanium, arsenic, antimony, uranium, or cerium, and in many cases no separation is necessary.

Cupferron can be used to precipitate vanadium in the quinquivalent state in 1N sulfuric acid solution, but it is not selective, since iron, zirconium, titanium, and other elements are precipitated.⁸

The use of chloroform to extract cupferrates has proved very useful, chiefly as a method of removing vanadium and other elements that would interfere in the determination of uranium.^{9,10} This method has been used to concentrate vanadium and other members of the cupferrate group for spectrographic analysis.¹¹

One of the most satisfactory methods for the separation of various elements from vanadium is electrolysis with a mercury cathode in dilute sulfuric acid.¹² This method separates vanadium from iron, chromium, cobalt, nickel, copper, and molybdenum, but not from uranium, aluminum, and phosphorus.

Ammonium carbonate is not satisfactory for separating vanadium from uranium.¹⁴ It must also be noted that vanadium may be carried down with insoluble phosphates.⁷

Vanadium is partially extracted with ethyl ether¹⁵ from a nitrate-nitric acid solution.¹⁷

1.3 Methods of Determination. The following methods have been used for macro amounts of vanadium: (1) for material assaying 90 per cent vanadium pentoxide, oxidation by means of nitric acid, followed by reduction with ferrous sulfate, potentiometric methods being used for the end point; (2) for ores and sands, titration of vanadate ion with ferrous sulfate, or reduction with ferrous sulfate followed by permanganate titration.^{8,18}

For moderately small amounts the peroxide colorimetric method has proved satisfactory.¹⁹ For micro amounts the spectrophotometric determination of phosphotungstovanadic acid²⁰ is useful. Although the chloroform extraction of the oxinate^{3,21} furnishes a sensitive test, the pH for the separation from uranium is critical. The copper-spark spectrographic method is quite sensitive, as well as the carrier-distillation method. For low concentrations the cupferron extraction method prior to spectrographic analysis is excellent.⁶

The range of the various methods is given in Table 19.1.

(a) **Gravimetric Methods.** The ignition of ammonium vanadate to vanadium pentoxide for standardization purposes has been used. The sample is ignited at 500°C to constant weight. On heating to 658°C vanadium pentoxide will melt but will not volatilize.

(b) **Volumetric Methods.** (1) **Permanganate Method.** A standard method that has been useful for routine control on carnotite-bearing sands and mill concentrates is as follows:^{18,22}

Procedure. An appropriate amount of the sample (100 mesh or finer) is treated in a 250-ml beaker with 20 to 30 ml of sulfuric acid (1 to 1), 10 ml of nitric acid, and 2 to 10 ml of hydrofluoric acid. It is stirred well, covered, and evaporated gently to dense fumes of sulfur trioxide. If the nitric acid does not oxidize the sample com-

pletely, perchloric acid is also used. The solution is cooled, 75 ml of hot water is added and stirred well, and the mixture is heated at a temperature of 80 to 90°C until all soluble salts are in solution. It is then diluted until the solution is 8 per cent by volume in sulfuric acid, an excess of 0.5 per cent potassium permanganate solution is added, and the solution is cooled to 18 to 20°C.

A ferrous sulfate solution (80 g per liter) is run in until a slight excess is shown by testing a drop of the solution on a spot plate with a drop of 0.1 per cent potassium ferricyanide solution; an excess of 3 to 5 ml of ferrous sulfate is added, and the mixture is stirred and allowed to stand for 1 to 2 min. Five to six milliliters of freshly prepared cold solution of 15 per cent ammonium persulfate is added, and

Table 19.1—Methods for Determination of Vanadium

Method	Reagent	Weight	Concentration, ppm
Volumetric	Reduction or oxidation	≥0.5 mg	
Spectrophotometric	Hydrogen peroxide	0.2–15 mg	
	Oxine	10–250 γ	
	Phosphotungstic acid	10–250 γ	
Spectrographic	Copper spark	0.005–5 γ	
	Carrier distillation		≥5
	Cupferrate extraction		≥1

the mixture is stirred well and allowed to stand for a minute. The test is repeated with a drop of potassium ferricyanide solution, which indicates when the excess ferrous sulfate is oxidized, and the solution is titrated immediately with a standard permanganate solution to the usual pink end point, which remains permanent for 1 min. A blank on vanadium-free sand is run through all the steps of the procedure.

(2) Ferrous Sulfate Method. This standard method, or a modification of it, has been used for the determination of vanadium in ores and sands, black oxide, and mill concentrates.^{10,24,25} Chromium interferes if present, but it was not encountered in this class of materials. The procedure for black oxide is as follows:

Procedure.²⁴ A 10-g sample is mixed with water, and 10 ml of nitric acid (1 to 1) is added. The sample is covered with a watch glass and heated on the hot plate at low heat for at least an hour. Twenty milliliters of sulfuric acid (1 to 1) is added and mixed well with the sample. The beaker is then covered with a Speedyvap and heated at low heat for 4 hr. The heat is increased until sulfur trioxide fumes

are evolved. The sample is cooled, the sides of the beaker are washed down with water, and the sample is fumed again. Four fumings, with intermittent cooling and washing with water, are necessary. After the last fuming the sample is cooled, 85 ml of water and enough sulfuric acid (1 to 1) to make the solution approximately 10 per cent acid are added, and the sample is digested on the steam bath for 1 hr. The solution is filtered through a Whatman No. 40 filter paper, and the insoluble material is washed thoroughly with hot water until the filtrate is about 200 ml. The solution is evaporated to 100 ml and cooled to room temperature before titration. Enough 0.1N potassium permanganate solution is added dropwise to produce a pink color in the solution. The solution is allowed to stand a few minutes, and then the excess potassium permanganate is reduced by the careful addition of 0.1N sodium nitrite solution. When the pink color has just disappeared from the solution, exactly 4 drops more of the sodium nitrite solution is added in excess. The sides of the beaker are washed down with water, and 2.00 g of urea is added. The solution is stirred for 30 sec and set aside for 10 min. Ten milliliters of 85 per cent phosphoric acid and 7 drops of indicator are added. (Indicator solution: 90 ml of water is added to 0.32 g of barium diphenylamine sulfonate and 0.5 g of anhydrous sodium sulfate; the indicator solution is allowed to stand overnight and is filtered and diluted to 100 ml.) The solution is stirred and then titrated with ferrous ammonium sulfate solution until the purple color changes to a clear green.

(3) Potentiometric Ferrous Sulfate Method. Commercial sodium vanadate has been analyzed by this standard method.^{26,36} Reducible substances must be absent. There were no interfering elements in the materials analyzed.

Procedure. A 1.5-g sample of sodium vanadate is weighed into a 250-ml beaker and moistened with water, and 20 ml (1 to 1) of sulfuric acid is added. The solution is heated until sulfur trioxide fumes are evolved; then it is cooled. A mixture of 50 ml of water and 10 ml of (1 to 1) sulfuric acid is added; then it is heated on a hot plate until solution is completed. The solution is cooled, transferred to a 250-ml volumetric flask, made to volume at room temperature, and shaken well. Three separate 50-ml aliquots are taken from each flask and placed in 400-ml beakers. To each beaker are added 40 ml of nitric acid, 25 ml of sulfuric acid, and enough water to bring the volume to 250 ml. Some glass beads are added to the beaker, which is then covered with a watch glass and placed on an electric heater. The solution is boiled so that its volume is decreased to 100 ml by steady boiling for 1 hr. It is then removed from the heater, made up to 300 ml, and cooled to 5°C.

The solution is titrated potentiometrically with the ferrous ammonium sulfate solution by using a platinum and calomel electrode setup and a vacuum tube voltmeter. The ferrous sulfate solution must be standardized for each set of determinations against a sample of ammonium metavanadate of known purity, which is carried through the given procedure with the regular samples.

(c) Colorimetric Methods. (1) Peroxide Method. Hydrogen peroxide reacts with vanadium(V) to form a reddish-brown complex, which has been used for the colorimetric determination of vanadium in black oxide.^{2,16} The maximum absorption occurs at $450\text{ m}\mu$, but in order to avoid interference due to uranium the transmittancy measurements are made at $530\text{ m}\mu$.

Hydrofluoric acid prevents the interference of titanium and decreases the interference of iron. Tungsten, chromium, nickel, and molybdenum also interfere, but in the black oxide samples analyzed by this method these elements were not present in sufficient amount to cause error. With 10-cm cells the range is 0.2 to 0.5 mg of vanadium pentoxide, with an accuracy of about 5 per cent.

Procedure. The silica is removed with hydrofluoric acid, followed by fuming with 10 ml of sulfuric acid. The solution is diluted and oxidized with potassium permanganate. It is then cooled, 0.5 ml of 30 per cent hydrogen peroxide and 2 ml of hydrofluoric acid are added, and the solution is made up to 100 ml with water. The solution is centrifuged, and the transmittancy is measured at $530\text{ m}\mu$ against a blank carried through the procedure, using a spectrophotometer with 10-cm cells.

(2) Phosphotungstate Method. In acid solutions vanadium(V) reacts with phosphate and tungstate to form a yellow complex phosphotungstovanadic acid.²⁸ The transmittancy is measured with a spectrophotometer in the range of 350 to $400\text{ m}\mu$.

Wright and Mellon have listed a large number of elements that interfere.²⁸ Findlay has given a procedure for the elimination of these interferences by a mercury cathode electrolysis, followed by cupferron extraction, while Cowan²⁹ has applied a cupferron extraction procedure to uranium samples. The method has been used for the range of 10 to $250\text{ }\gamma$ of vanadium with an accuracy of about 10 per cent. The following procedure has been used for the determination of vanadium in ash:

Procedure.²⁰ A sulfuric acid solution (8 to 92) containing approximately 10 to $250\text{ }\gamma$ of vanadium is fumed with perchloric acid to oxidize the vanadium. The solution is cooled, 0.5 ml of phosphoric acid is added to decolorize the iron, and the solution is then diluted to 25 ml. From the solution two 10-ml aliquots are transferred to 25-ml

volumetric flasks. One flask is diluted with water to the mark. Two milliliters of 4 per cent sodium tungstate solution is added to the other flask, which is then diluted to the mark. The transmittancy is measured at 500 $m\mu$ with a spectrophotometer (uranium interferes at this wavelength). A reagent blank, determined for all the reagents, is run through the entire procedure at the same time.

(3) Oxine Method.^{3,16,21} The red color formed when vanadium oxyquinolate is complexed with ethyl alcohol can be extracted by chloroform. The transmittancy of the solution is measured at 475 $m\mu$ after interfering elements have been removed.

The only element likely to interfere in the determination is iron, which may be conveniently removed. Analyses have been successfully carried out in the presence of copper, calcium, iron, aluminum, titanium, molybdenum, chromium, lead, tantalum, tin, bismuth, and tungsten.

The oxine method is especially suited to a range of 20 to 100 γ of vanadium.

Procedure.³ The weighed sample is dissolved in 70 per cent perchloric acid. If the compound is a uranium halide, a reflux condenser is used and washed down after solution of the salt is complete. In most cases heat is necessary to effect solution. The solution is transferred to a 100-ml beaker, and ammonium hydroxide is added until a permanent precipitate forms. This precipitate is dissolved with nitric acid, and a sufficient excess of acid is added to adjust the pH to 1.4. The solution is transferred to a separatory funnel (the solution should have a volume of approximately 100 ml at this point). One-tenth of a gram of cupferron dissolved in several milliliters of water is added and mixed thoroughly. The solution is extracted with three portions of chloroform, and the extract is filtered through a Whatman No. 40 filter paper. The chloroform solution is evaporated to dryness on the hot plate, 1 ml of nitric acid and 2 to 3 ml of perchloric acid are added, and the beaker is covered with a watch glass and digested on the hot plate until the solution is clear. The watch glass is removed, and the solution is evaporated to dryness. One milliliter of 1N sodium hydroxide is added, and the solution is diluted to approximately 25 ml. Digestion is carried out on the hot plate for 15 to 20 min. The sodium hydroxide solution is filtered through a Whatman No. 42 filter paper, which is thoroughly washed. The combined filtrate and washings should amount to 50 to 75 ml. Eight drops of oxine solution (5 g of oxine dissolved in 10 ml of acetic acid and diluted to 100 ml) and 15 ml of ethyl alcohol are added. The pH of the solution is adjusted to 4.5 with 1N sulfuric acid and 1N sodium hydroxide. The red color of the vanadium oxyquinolate-alcohol complex is extracted with three

5- to 8-ml portions of chloroform. These extracts are filtered into a 25-ml volumetric flask and then diluted to the mark with chloroform. The transmittancy of the solution is measured at 475 m μ .

2. COLUMBIUM AND TANTALUM

Analyses for columbium and tantalum have been made chiefly in the determination of small amounts of these elements in uranium-base materials. Occasion has arisen for analysis of columbium-uranium, tantalum-uranium, and tantalum-thorium alloys, as well as a few ores. The separation of columbium from tantalum was not necessary. The general analytical chemistry of columbium and tantalum has been adequately reviewed and need not be discussed here.³⁰

Macro amounts of columbium and tantalum are usually determined by precipitation as the tannin or cupferron complex, followed by ignition to the oxide.^{8,30} In most instances titanium will appear as an impurity, but it can be determined colorimetrically.

Micro amounts have usually been determined by spectrographic means either directly³¹ or in the cupferrate group obtained by chloroform extraction.¹¹ Tantalum has been determined spectrographically in columbium after a tannin concentration.⁵

2.1 Solution of Samples. Compounds of columbium and tantalum can be brought into solution by hydrofluoric acid, pyrosulfate fusion, or alkaline fusion. The decomposition of a mineral or ore may be a tedious operation, depending upon the material.⁸ Uranium alloys may be dissolved with nitric acid and hydrofluoric acid.

When a uranium-tantalum alloy is treated with nitric acid, the tantalum remains insoluble. A particular sample so treated containing about 3 g of uranium, was evaporated to the crystallization stage. The uranyl nitrate was extracted with ether, and the remaining aqueous solution was carried through a tannin precipitation procedure, but no yellow tantalum precipitate was obtained,³² the negligible solubility of tantalum in nitric acid thus being indicated.

Thorium-tantalum alloys may be treated with hydrochloric or nitric acid and sodium fluosilicate. This procedure dissolves the thorium and leaves the tantalum undissolved.³³

2.2 Methods of Separation. The method of separation used on ores was essentially the method given in Hillebrand and Lundell.⁸ Cupferron may be used to separate columbium and tantalum from several other elements, but it is not specific. The chloroform extraction of the cupferrates for large amounts of columbium is not very satisfactory owing to the low solubility of columbium cupferrate.

2.3 Methods of Determination. Columbium and tantalum are most often precipitated in a form that can be converted to oxide on ignition. Tannin is one of the most common precipitants used. For the separate determination of columbium and tantalum the method of Schoeller and Powell is applicable.³⁰

The gravimetric method³⁴ is useful for routine control analysis on uranium alloys. Results are low, but a correction can be made.

Other workers have employed a gravimetric method for uranium-tantalum alloys based on preliminary treatment of the alloy with nitric acid, whereupon the tantalum remains undissolved. The residue is dissolved by fusion, and the tantalum is precipitated with tannin in acid oxalate solution. The tannin precipitate³² is ignited to Ta_2O_5 .

The insolubility of tantalum in nitric or hydrochloric acid has also been employed in analyzing thorium-tantalum alloys. The thorium is dissolved in nitric or hydrochloric acid and sodium fluosilicate, the tantalum being left insoluble. The tantalum is filtered off, ignited, and weighed, while the thorium is precipitated as oxalate.³⁴

The copper-spark spectrographic method will detect 0.02 γ of columbium or 0.1 γ of tantalum in a solution. The cupferron chloroform extraction method has been used extensively for the determination of low concentrations in uranium-bearing material. The limit of detection is 3 ppm for columbium and 40 ppm for tantalum.⁶ Nephelometric methods have been used in other laboratories,³⁵ with phenylarsenious acid being employed to precipitate columbium and tantalum.

(a) Gravimetric Methods. (1) Determination of Columbium or Tantalum in Uranium Alloys. Columbium or tantalum, when fumed with perchloric acid, is dehydrated and precipitated as oxide. The precipitate can be ignited and weighed. This procedure is applicable only to uranium alloys with one earth present. The columbium results may be low by as much as 5 mg. When solubility correction is made,¹⁵ results accurate to 0.5 mg may be expected. Uncorrected tantalum results should be accurate within 1 to 2 mg.

Procedure.³³ The sample, enough to give 50 to 200 mg of the metal oxide, is decomposed with 25 ml of nitric acid and 2 to 3 ml of hydrofluoric acid. If uranyl fluoride precipitates, it may be redissolved by dilution with water. When the metal is decomposed, 40 ml of 70 per cent perchloric acid is added, and the sample is evaporated to fumes. If uranium tetrafluoride is still present, the addition of more acid and water, followed by fuming, is necessary until a clear solution results. The sample is evaporated once more and fumed strongly for 10 to 15 min on a hot plate. Longer fuming does not improve recovery. The mixture is diluted to about 200 ml and, after the addition of filter pulp, is warmed and allowed to stand overnight. The solution is filtered

through a Whatman No. 42 filter paper, and the residue is washed at least 12 times with hot hydrochloric acid (1 to 20). This washing is necessary to remove perchloric acid and to prevent small explosions on ignition. The sample is ignited in a muffle at 1000°C and weighed as Cb_2O_5 or Ta_2O_5 .

(2) Determination of Tantalum in Tantalum-Thorium Alloys. This determination is based on the insolubility of tantalum in nitric acid and sodium fluosilicate.³³ About 450 ml of concentrated nitric acid is added to the sample. When the mixture begins to boil, approximately 8 mg of sodium fluosilicate is added, and the boiling is continued, with acid added if necessary to keep the volume at about 350 ml. The solution is cooled, diluted to 450 ml, and filtered. The residue is washed with water and ignited to Ta_2O_5 .

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Chapter 20

TITANIUM, ZIRCONIUM, AND HAFNIUM

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The determination of titanium, zirconium, and, to a lesser extent, hafnium has been of interest because of the presence of these elements as impurities.

1. TITANIUM

Since titanium usually occurs as a trace element, colorimetric methods were employed extensively in its determination. Several reagents including hydrogen peroxide,¹⁻³ dihydroxymaleic acid,^{4,5} and disodium 1,2-dihydroxybenzene-3,5-disulfonate,⁶⁻⁸ produce colors suitable for spectrophotometric determination. Spectrographic methods⁹ have also been employed for the determination of traces of titanium after a chemical separation from the major interfering elements. These methods are discussed in Chap. 26 on "Spectrochemical Methods."

Macro methods for the determination of titanium have been of interest. Suitable volumetric and gravimetric methods are discussed in standard analytical works, such as those of Hillebrand and Lundell,¹ Schoeller and Powell,¹⁰ and "Scott's Standard Methods of Chemical Analysis."¹¹

1.1 Solution of Samples. Alloys of titanium with uranium or thorium are first decomposed with hydrochloric acid and then oxidized by the addition of nitric acid. Most minerals and other difficultly soluble materials may be decomposed in a mixture of hydrofluoric and sulfuric acids. In particularly stubborn cases fusion with potassium pyrosulfate or, preferably, acid fluoride is recommended.^{1,11}

Uranium oxides may be dissolved by a mixture of nitric and sulfuric acids. The solution is then evaporated until fumes of sulfur

trioxide are given off. The fuming is necessary to ensure the solution of titanium oxide, which is practically insoluble in other acids.

It must be remembered that solutions of titanium tend to hydrolyze quite readily. It is therefore preferable to work with solutions in 5 to 10 per cent sulfuric acid.

1.2 Methods of Separation. Titanium was determined by the colorimetric peroxide method, in which it was usually unnecessary to separate titanium in the pure state, a separation from uranium ordinarily being sufficient.

Cupferron affords a good separation of titanium from many elements, including uranium, chromium, nickel, and aluminum.^{1,3,12} Extraction of the metal cupferrates with chloroform¹³ has been found useful for the recovery of traces of titanium. Vanadium, iron, molybdenum, and tungsten, which interfere with the peroxide method of determination, also form insoluble cupferrates.

Titanium may also be separated from uranium by precipitation of uranium peroxide with hydrogen peroxide at a pH of 3 to 4.^{14,15}

Combinations of the above separations have been employed for the analysis of uranium materials for titanium.

1.3 Methods of Determination. Except for spectrographic methods, which are discussed in Chap. 26 on "Spectrochemical Methods," the usual occurrence of titanium as a trace element has limited the choice of analytical methods for this element to spectrophotometric methods.

The hydrogen peroxide method has been widely used. It is rapid and accurate and has but few interferences, most of which are inconsequential in pure uranium materials.

The dihydroxymaleic acid method is more sensitive than the hydrogen peroxide method and offers the advantage that vanadium does not interfere.

The use of disodium 1,2-dihydroxybenzene-3,5-disulfonate permits the determination of titanium in the presence of a large excess of uranium.

Spectrographic methods are useful because they generally require only group separations and because it is possible to determine several additional elements simultaneously.

(a) **Colorimetric Methods.** Of the methods described below, the hydrogen peroxide method has had wide and varied application (see references 2, 3, 12, 14-19); dihydroxymaleic acid⁴ has been adapted primarily to a particular class of materials; and the use of disodium 1,2-dihydroxybenzene-3,5-disulfonate^{6,7,8} has undergone considerable experimental investigation, but has had rather limited application to routine analysis.

(1) Hydrogen Peroxide Method. In this method hydrogen peroxide is added to a 5 to 10 per cent sulfuric acid solution of the sample, from which interfering elements have been removed. The spectral transmittancy of the color produced is measured spectrophotometrically at the wavelength of maximum absorption.²⁰

Traces of fluoride will bleach the titanium color completely, but this interfering ion is rather easily eliminated by fuming with sulfuric acid. Iron, nickel, and uranium interfere because of their colors, but the effect of these elements when present in low concentration may be largely compensated by a blank in which the titanium color

Table 20.1—Methods for Determination of Titanium

Method	Reagent	Range
Spectrophotometric	Hydrogen peroxide	2 – 30 ppm
Spectrophotometric	Dihydroxymaleic acid	0.5 – 2.5 ppm
Spectrophotometric	Disodium 1,2-dihydroxy- benzene-3,5-disulfonate	0.5 – 3.0 ppm
Spectrographic	Cupferrate concentration	3 – 160 ppm
Spectrographic	Copper spark	0.005 – 1 γ

has not been developed. Vanadium, molybdenum, tungsten, and chromium produce colors with hydrogen peroxide and must be removed. Certain other elements interfere if present in large concentrations.¹

Cupferron Separation Procedure.^{3,18} The sample is dissolved in nitric acid, evaporated, and baked on a hot plate. The oxides are dissolved in 10 per cent sulfuric acid, which is boiled to ensure complete solution. Potassium permanganate solution (1 g per liter) is added dropwise until a permanent pink color is observed. After cooling, the solution is transferred to a separatory funnel, and cold 6 per cent cupferron solution is added. The funnel is shaken, and the precipitated metal cupferrates are then extracted with chloroform. Precipitations with cupferron are repeated until the chloroform layer appears colorless or very pale blue. The combined chloroform extracts are placed in a large silica crucible, to which is added enough water to cover the surface of the chloroform. The liquids are then gently evaporated to dryness on a steam bath.

A small amount of insoluble material often remains at the interface of the water and chloroform layers during extraction. Therefore, after the extraction is complete, the interface, together with a small amount of the acid layer above it, is drawn off and filtered through a Whatman No. 40 filter paper. The paper is washed thoroughly with

2 per cent sulfuric acid and placed in the crucible containing the decomposed cupferrates, which remain after the evaporation of the chloroform. The residue is then ignited at a slowly increasing temperature, with final ignition at 600 to 700°C.

The residue remaining in the crucible is fused with potassium pyrosulfate, which, after cooling, is partially dissolved in a small amount of water and transferred to a beaker. Fifty milliliters of 5 per cent sodium hydroxide is added, and the sample is boiled to dissolve the melt and to coagulate any precipitate. If no precipitate forms, 1 mg of iron is added as a carrier for the titanium. The solution is then filtered through a Whatman No. 42 filter paper, which is washed with hot 0.5 per cent sodium hydroxide solution.

The precipitate is dissolved, and the filter is washed with hot 10 per cent sulfuric acid. The solution is cooled and diluted to 50 ml in a volumetric flask. A 20-ml aliquot is pipetted into a 25-ml volumetric flask, 0.2 ml of 30 per cent hydrogen peroxide is added, and the solution is diluted to 25 ml.

The transmittancy of this solution is measured spectrophotometrically at 400 $m\mu$ by using as a reference blank a sample which has been carried through the procedure but which contains no hydrogen peroxide. The amount of titanium present is determined from a concentration-transmittancy curve constructed from measurements on a series of standards containing known amounts of titanium dissolved in 25 ml of 10 per cent sulfuric acid and containing 0.2 ml of 30 per cent hydrogen peroxide. The curve follows Beer's law over a large range of concentration.

Peroxide Separation Procedure.^{2,14} In the case of essentially pure uranium materials the sample is dissolved in dilute nitric and sulfuric acids, and the solution is evaporated until fumes of sulfur trioxide are no longer evolved. The sulfates are dissolved in dilute sulfuric acid, and the uranium is precipitated at pH 3 to 4 by adding hydrogen peroxide to a cold solution. After centrifuging, the supernatant liquid is evaporated to fumes of sulfur trioxide and diluted to 100 ml in a volumetric flask with 10 per cent sulfuric acid. Two 20-ml aliquots are transferred to 25-ml flasks. To one flask 2 ml of 30 per cent hydrogen peroxide is added, and the solutions in both flasks are diluted to 25 ml. The transmittancies of the two solutions are measured spectrophotometrically at 400 $m\mu$, the solution containing no peroxide being used as a reference blank. The amount of titanium present is determined from a concentration-transmittancy curve constructed from measurements on a series of standard uranium solutions which contain varying amounts of titanium and which have been carried through the above procedure. As indicated in Fig. 20.1, this curve is

about 7 per cent higher than a curve constructed from standards containing no uranium.

If vanadium or molybdenum is present in the sample, it may be removed by the following method: After the filtrate from the peroxide

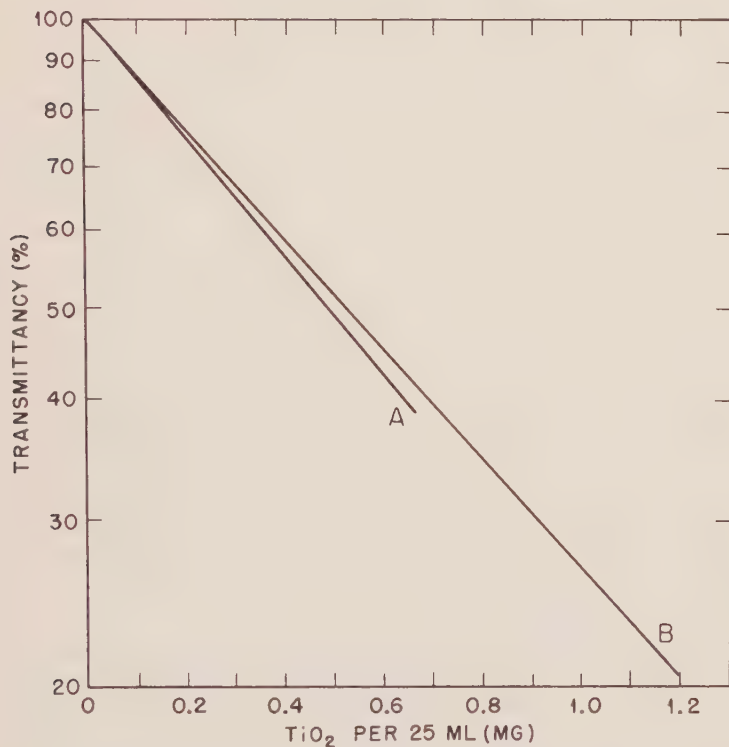


Fig. 20.1 — Concentration-transmittancy curve for the determination of titanium with hydrogen peroxide. A, solutions prepared by dissolving known amounts of titanium in 10 per cent H_2SO_4 , adding 2 ml of 30 per cent H_2O_2 , and diluting to 25 ml; B, solutions prepared by adding known amounts of titanium to pure uranium solutions and carrying the solutions through the procedure. Measurements made at 400 $\text{m}\mu$ against a sample containing no H_2O_2 .

precipitation has been fumed with sulfuric acid, it is diluted to 100 ml, and a few milligrams of ferric chloride or ferric sulfate is added. Excess acid is nearly neutralized with sodium hydroxide, and the solution is poured into 150 ml of 1N sodium hydroxide solution. The precipitate is filtered, washed with 0.5N sodium hydroxide solution, ignited, and dissolved by fusion with about 2 g of potassium pyrosul-

fate. The melt is dissolved and diluted to 100 ml in a volumetric flask with 10 per cent sulfuric acid. The analysis is then continued as above.

(2) Dihydroxymaleic Acid Method. The basis of the dihydroxymaleic acid method is the formation of a yellow-orange color by the reaction of dihydroxymaleic acid with titanium ion in slightly acid solution. The color is dependent upon the acidity and upon the time of standing, and these conditions must be standardized. Vanadium, calcium, aluminum, fluorine, chromium, magnesium, and nitric acid do not interfere. Ferric ion interferes, but the addition of hydroxylamine hydrochloride eliminates the interference by reducing iron to the ferrous state and at the same time tends to stabilize the titanium color.

Procedure.⁴ This method has been applied to the analysis of ash. An appropriate size of sample is ashed, and the ash is dissolved in sulfuric acid. The solution is transferred to a 100-ml volumetric flask and diluted to volume. An aliquot of the solution containing 10 to 60 γ of titanium is transferred to a 25-ml volumetric flask, and 10 ml of water and a drop of phenolphthalein indicator are added. The solution is made just alkaline with sodium hydroxide, as indicated by the phenolphthalein, and adjusted to a pH of 3 with 6N sulfuric acid, as indicated by Hydrion paper or a similar indicator. The solution is then diluted and cooled, and 1 ml of 10 per cent hydroxylamine hydrochloride solution is added. After mixing the contents of the flask, 1.00 ml of freshly prepared dihydroxymaleic acid solution (0.2 g of dihydroxymaleic acid dihydrate in 25 ml of absolute ethyl alcohol) is added, and the sample is diluted to volume. The solution is allowed to stand for 25 min, after which the transmittancy is measured spectrophotometrically at 400 $m\mu$ within 10 min by using as a blank a solution of sample containing no developing reagent. The amount of titanium present is determined from a standard concentration-transmittancy curve. Beer's law is obeyed up to a concentration of 60 γ of titanium in 25 ml of solution.

2. ZIRCONIUM

Micro and macro analyses were made for zirconium. For macro analyses gravimetric methods were employed. Cupferron^{21,22} and phenylarsonic acid²³ were used as precipitants, and in both cases the precipitate was ignited and weighed as zirconium oxide. Micro determinations were performed spectrophotometrically by using either alizarin²⁴ or *p*-dimethylaminoazophenylarsonic acid^{25,26} as color reagents. Spectrographic methods⁹ were also developed. They are discussed in Chap. 26 on "Spectrochemical Methods."

2.1 Solution of Samples. Various fluxes have been suggested for decomposing zirconium minerals and other zirconium materials soluble only with difficulty. These include fusion with sodium peroxide in a sodium carbonate-lined nickel crucible, potassium pyrosulfate, potassium acid fluoride, and borax.¹¹ The proper choice of flux will depend upon the nature of the material being attacked.

Treatment of zirconium alloys will depend largely upon the other constituents of the alloy and upon the subsequent treatment of the sample after it is dissolved.

Solutions of zirconium hydrolyze very readily and will precipitate, often colloiddally, from solutions that are not strongly acidic, unless a complexing reagent is present. This hydrolysis may not be noticed, particularly with small concentrations, and aliquot samples taken for analysis may not be representative. Heating such solutions for several minutes with strong mineral acid before aliquot portions are measured has been found to improve the precision of analysis of some such solutions.

2.2 Methods of Separation. No specific reagents for zirconium are known, with the possible exception of phosphate under the proper conditions.

Cupferron, although not specific, quantitatively precipitates zirconium in cold 10 per cent acid solution. Tartaric and boric acids do not interfere, and the precipitate may be ignited to zirconium oxide. Arsenic acid and various organic derivatives such as phenylarsonic acid have found considerable use as precipitants for zirconium. The precipitate may be ignited to the oxide, but, unless the ignition is continued for a long time at a high temperature, it may be contaminated with arsenic. Uranium, thorium, titanium, cerium, tungsten, iron, columbium, and tantalum may be coprecipitated, and two or more precipitations may be required.

Detailed treatments of these and other separations are given in standard analytical texts.^{1,10,11}

2.3 Methods of Determination. For macro amounts of zirconium, precipitation with cupferron gives fairly good results. In general, more than one precipitation is required, or the use of a different precipitant is necessary in order to remove a number of interferences. Of the colorimetric methods described below, the alizarin method, although not so sensitive as the pararsonic (*p*-dimethylaminoazophenylarsonic) acid method, has given the least difficulty in actual practice. Spectrographic methods are convenient from the standpoint of simultaneous determination of a number of elements. The accuracy of spectrographic methods parallels the precision of spectrophotometric methods for trace amounts.

(a) Gravimetric Methods. (1) Cupferron-Phenylarsonic Acid Method. A method has been proposed by Bricker²³ for the gravimetric determination of zirconium in uranium. It consists of precipitating zirconium with cupferron,¹ igniting the precipitate to the oxide, dissolving the oxide by fusion with potassium pyrosulfate, and precipitating zirconium with phenylarsonic acid.²⁷ The precipitate formed is

Table 20.2—Methods for Determination of Zirconium

Method	Reagent	Range
Gravimetric	Cupferron-phenylarsonic acid	50 – 200 mg
Gravimetric	Barium nitrate and hydrofluoric acid, cupferron	50 – 150 mg
Colorimetric	<i>p</i> -Dimethylamino-azophenylarsonic acid (pararsonic acid)	0.1 – 0.7 ppm
Colorimetric	Alizarin	1 – 5 ppm
Spectrographic	Cupferrate concentration	3 – 160 ppm
Spectrographic	Copper spark	0.01 – 10 γ

ignited to zirconium oxide and weighed. The method has not been subjected to rigorous test by extensive use. The interfering substances would include only those elements precipitated by both reagents.

Procedure.²³ A 5-g sample of the metal is ignited in a silica dish. The oxide is dissolved in 20 ml of water, 3 ml of nitric acid, and 3 ml of sulfuric acid, and the solution is evaporated to fumes of sulfur trioxide and cooled. To it are added 5 ml of water and 3 ml of hydrofluoric acid. The solution is stirred, and most of the sulfuric acid is fumed off. The residue is dissolved in 50 ml of 10 per cent sulfuric acid and cooled in ice. At least 5 ml of 5 per cent cupferron solution is added. When precipitation is complete, the solution is filtered. The precipitate is washed 12 times with 10-ml portions of 10 per cent hydrochloric acid and five times with portions of 3N ammonium hydroxide. The precipitate is ignited carefully at first and finally at full heat in a quartz crucible. The residue is fused with 1 g of potassium pyrosulfate and dissolved in 50 ml of sulfuric acid (1 to 10). If titanium is present, 3 ml of 30 per cent hydrogen peroxide is added. The zirconium is precipitated with 5 ml of 5 per cent phenylarsonic acid, filtered, and washed with 0.25N sulfuric acid containing a little phenylarsonic acid and hydrogen peroxide. The filter paper is transferred

to the original beaker in which the precipitation was made and is digested with 5 ml of concentrated hydrochloric acid. The solution is diluted to 50 ml. To it is added 2 or 3 ml of 5 per cent phenylarsonic acid. The precipitate is filtered, washed with several portions of 0.25N hydrochloric acid, ignited, and weighed as ZrO_2 .

(2) Barium Zirconium Fluoride-Cupferron Method. Tertiary alloys of uranium-zirconium-columbium in which both zirconium and columbium were to be determined have caused some difficulty, but a method developed by Hume²¹ has been adapted for gravimetric analysis.²⁸ The sample is dissolved by treating it first with nitric acid to dissolve the uranium and then with hydrofluoric acid to dissolve the zirconium and columbium. Zirconium is precipitated as BaZrF_6 , the precipitate is dissolved in boric acid-hydrochloric acid solution, and the zirconium is precipitated with cupferron. The precipitate is ignited and weighed as zirconium oxide. Interfering elements were not present in larger than micro amounts.

Procedure.²⁸ An appropriate size of sample is one containing 50 to 150 mg of zirconium. The sample taken is cleaned, weighed, and treated in a platinum dish with 50 ml of concentrated nitric acid. The dish is covered with a watch glass and heated on the hot plate at low heat until no further action is observed. The uranium should be completely in solution before further action is taken. The solution is evaporated to about 20 ml in order to remove the excess nitric acid and is then diluted to 40 ml with water. One milliliter of hydrofluoric acid is added, and the solution is stirred with a platinum rod. If all the columbium and zirconium do not dissolve, a few more drops of hydrofluoric acid are added with continued stirring. Uranyl fluoride will precipitate if too much hydrofluoric acid is added, but it may be redissolved with a little more water. To the cool, clear yellow solution are added 20 ml of 5 per cent barium nitrate solution per 0.1 g of zirconium present and 3 ml of hydrofluoric acid. The mixture is stirred with a platinum rod, and then the precipitate is allowed to settle until the supernatant liquid is perfectly clear. A few milliliters of barium nitrate and a few drops of hydrofluoric acid are added to test the completeness of precipitation. If no more precipitate forms, the contents of the dish are filtered by using a Whatman No. 42 filter paper and a waxed glass or bakelite funnel and beaker.

The inside of the dish is carefully policed to remove the last traces of the precipitate. The precipitate is washed three or four times with small portions of water to remove most of the uranium, and the filter paper is transferred to a 400-ml beaker containing 20 ml of 5 per cent boric acid solution, 20 ml of concentrated hydrochloric acid, and about 150 ml of water. The suspension is heated nearly to boiling for

15 min with frequent stirring to disintegrate the paper and to decompose the precipitate. The beaker is then cooled in an ice bath to about 5°C, and 25 ml of 6 per cent cupferron solution is added for each 0.1 g of zirconium present. The precipitate is filtered by using a platinum filter cone and slight suction and is then washed six to eight times with 1N hydrochloric acid containing a few drops of cupferron solution. The filtrate is tested for completeness of precipitation with a few milliliters of cupferron solution. The precipitate is transferred to a weighed porcelain crucible and is dried. The precipitate is then ignited, carefully at first to burn off organic matter and finally at full blast. The crucible is cooled, and the precipitate is weighed as zirconium oxide.

(b) Colorimetric Methods. (1) Pararsonic Acid Method. A colorimetric method for zirconium proposed by Nazarenko,²⁹ further developed by Hayes and Jones³⁰ and adapted for the determination of micro amounts of zirconium in solutions,^{25,26} consists in precipitating zirconium with pararsonic (*p*-dimethylaminoazophenylarsonic) acid, filtering the precipitate, and decomposing it with ammonium hydroxide. The transmittancy of the resulting solution is measured spectrophotometrically at 450 m μ (Fig. 20.2). Beer's law is obeyed. Interfering elements include thorium, fluorine, phosphate, sulfate, and nitric acid, and a special procedure is used to remove these interferences. The method is satisfactory in the range of 0.1 to 7 γ and is accurate within 5 per cent.

Procedure.²⁶ The sample solution (0.1 ml) is added to 1 ml of 1 per cent hydrochloric acid in a 20-ml beaker and diluted to 3 ml with 1 per cent hydrochloric acid. To the solution are added 1 ml of 6N hydrochloric acid, several drops of hydroxylamine hydrochloride, and 1 ml of 0.1 per cent pararsonic acid (prepared by dissolving 0.1 g of pararsonic acid in 100 ml of 95 per cent ethyl alcohol containing 5 per cent hydrochloric acid, shaking, allowing to stand overnight, and filtering through a fine glass filter covered with an asbestos mat). The solution is agitated, allowed to stand for 5 min, and filtered with suction through a fine glass filter covered with a mat of fine asbestos about $\frac{1}{8}$ in. thick. Difficulty with the analysis is often traced to this filtration, which should be repeated several times if necessary. The precipitate is washed free of excess reagent with 1 per cent hydrochloric acid and is then dissolved through the filter with 1-ml portions of ammonium hydroxide (1 to 2) until the solution comes through colorless. It is then diluted to 10 ml with water, and its transmittancy is measured at 450 m μ with a spectrophotometer, distilled water being used as a blank. The method is standardized with known quantities of zirconium.

In the presence of interfering substances the following procedure is used: The sample solution (0.10 ml) is added to 4 ml of 2N hydrochloric acid in a small separatory funnel; 0.5 millimole of boric acid is added to the hydrochloric acid to reduce etching if much fluoride is present. Fifty micrograms of iron is added as a carrier. An excess of 6 per cent cupferron solution is added dropwise with agitation; 3 to 4 drops is usually sufficient. After 5 min the precipitate is extracted with 1 ml of chloroform, which is drained into a clean platinum crucible. Two more 1-ml portions of chloroform are used to

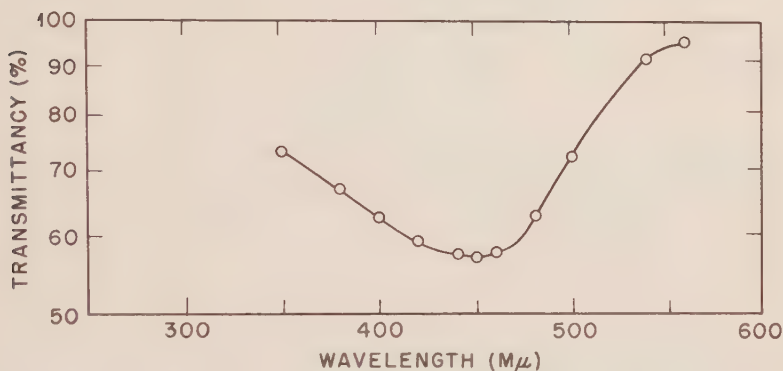


Fig. 20.2—Spectral transmittancy curve for the zirconium complex of *p*-dimethylaminoazophenylarsonic acid. Measurements made on a solution containing 4.95 γ of Zr per 10 ml, by using a Coleman model 11 spectrophotometer with 1.7-cm cuvettes; distilled water used as a blank.

wash out the funnel. The chloroform is removed by careful evaporation on a hot plate. When cool the residue is dissolved in 0.25 ml of sulfuric acid, 0.25 ml of nitric acid is added, and the oxidation is repeated. If all organic material has not been destroyed, the oxidation is again repeated. Then the residue is heated strongly to remove all sulfur trioxide. The zirconium is dissolved in 2 ml of 6N hydrochloric acid, evaporated to 1 ml, cooled, and transferred to a 20-ml beaker. The crucible is washed with 1 per cent hydrochloric acid. The procedure is then continued as described above.

(2) Alizarin Method. The use of alizarin in the colorimetric determination of zirconium was developed by Liebhafsky and Winslow.³¹ Alizarin forms strongly colored lakes with many cations at the proper acidity. The zirconium lake is stable at a relatively high acidity, as compared to lakes of other metals. Phosphate, sulfate, fluoride,

molybdate, tungstate, and organic hydroxy acids interfere. Titanium and thorium interference may be eliminated by using higher acidities, but at the expense of the sensitivity of the method. Other cations do not interfere if present in amounts comparable to the amount of zirconium present, but large amounts of ferric iron, chromium, cobalt, cadmium, copper, lead, and aluminum may cause error. Uranium in hundredfold excess causes small positive errors. The solution is

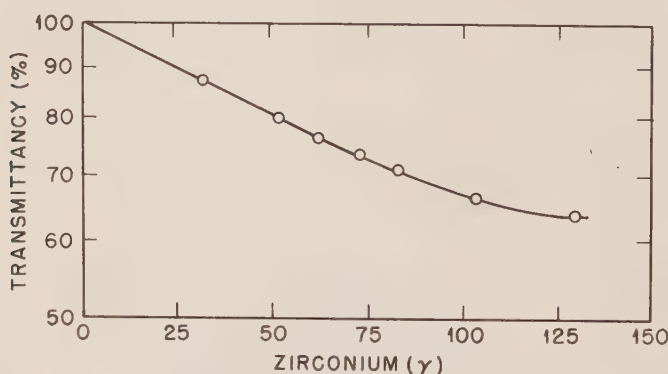


Fig. 20.3—Concentration-transmittancy curve for the determination of zirconium with alizarin. Measurements made on 25 ml of alcoholic solution containing 0 to 125 γ of zirconium and 0.5 ml of alizarin, by using a Beckman spectrophotometer at 570 $m\mu$ with 1-cm cells.

diluted with ethyl alcohol to stabilize the colloidal suspension. The most useful range of the method is 25 to 125 γ of zirconium, and the precision is about 5 per cent.

Procedure.²⁴ One milliliter of a sample containing not more than 100 γ of zirconium in hydrochloric or nitric acid solution is transferred to a 25-ml volumetric flask. Half a milliliter of alizarin solution, containing 0.125 g of alizarin in 100 ml of 95 per cent ethyl alcohol, is added, followed by ammonium hydroxide in sufficient quantity to produce a purple color. After 2 min the solution is neutralized with 1N hydrochloric acid, and 0.1 ml excess of 7N hydrochloric acid is added. The solution is then diluted to 25 ml with 95 per cent ethyl alcohol and is shaken. The transmittancy of the solution is measured spectrophotometrically at 560 $m\mu$ in 1-cm cells. The amount of zirconium present is determined from a concentration-transmittancy curve (Fig. 20.3).

(c) **Turbidimetric Methods.** One method²² for the turbidimetric determination of micro amounts of zirconium in uranium is of interest

and may be mentioned briefly. A 10-g sample of uranium is dissolved in hydrochloric acid, then nitric acid is added, and finally the solution is evaporated to dryness several times with hydrochloric acid. Cupferron solution is added, and the zirconium cupferrate precipitate is extracted with chloroform. The extract is evaporated to dryness, and the residue is fused with potassium pyrosulfate. The melt is dissolved, filtered, and diluted to 10 ml. One-milliliter aliquots are placed in test tubes, and a solution of phenylarsonic acid is added. After 10 min the tubes are compared in a light beam with standards similarly treated. Columbium and tantalum do not interfere, but more than 300 γ of tin or 25 γ of titanium does interfere. The method is useful in the range of 1 to 12 ppm of zirconium.

3. HAFNIUM

Hafnium has been determined in only a few cases, when spectrographic examination of cupferron group concentrates included an estimation of hafnium along with the other constituents of the concentrates.⁹

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Chapter 21

THE PLATINUM METALS

By G. W. Cressman and C. J. Rodden

1. INTRODUCTION

Uranium metal, as well as uranium compounds and ores, has been analyzed for traces of platinum, palladium, iridium, rhodium, ruthenium, and osmium. In some instances materials were analyzed for macro amounts of platinum.

The excellent monograph "The Platinum Metals," by Gilchrist,¹ gives a summary, together with references to the literature, of the methods used in the analysis of this group of metals.

1.1 Methods of Solution. Samples of uranium metal and uranium compounds are treated with a nitric-hydrochloric acid mixture, which dissolves platinum, palladium, and osmium. Metallic iridium, metallic ruthenium, metallic rhodium, and metallic osmium, when present as osmiridium, are insoluble. Inasmuch as the insoluble material is included in the concentrates examined spectrographically, no further attempt is made to dissolve these constituents. Uranium alloys in which uranium is the main constituent are dissolved in hydrochloric acid and 30 per cent hydrogen peroxide. Osmium is volatilized, but provision is made for a determination of this element.

The platinum in the catalyst material is readily soluble in aqua regia. Hydrochloric acid and sodium bromate are used to dissolve the platinum in the ores and residue examined.

Refractory materials of the platinum group may be dissolved by a method developed at the National Bureau of Standards.² The material is heated at an elevated temperature in a sealed glass tube, which contains a small amount of a suitable oxidizing agent, in contact with hydrochloric acid.

1.2 Group Separations. The procedure described by Gilchrist and Wichers³ is the best proved method for the separation of these elements from each other.

Reduction by hydrochloric acid and zinc serves for the separation of noble metals from solution.^{4,7} This principle is applied in the analysis of uranium-base materials to concentrate ruthenium, rhodium, palladium, iridium, and platinum, with gold used as the gathering agent. Osmium is volatilized in this procedure, in which the sample is dissolved in nitric acid, although it may be collected and determined colorimetrically if desired. The portion of the sample insoluble in the solution prepared for reduction is collected with the gold precipitate, and the mixture is examined spectrographically by

Table 21.1 — Limits of Detection

Element	Copper spark, γ	Spectrographic ^{4,8} method	
		Concentration using gold, ppm	Concentration by extraction, ppm
Ru	0.1	5	
Os			
Pd	0.05	5	0.5
Ir	0.5	100	10
Rh		20	2
Pt	0.02	1	5

complete volatilization in a d-c arc.⁵ In view of the incomplete precipitation of the sample, especially of the iridium, standard samples containing added amounts of the platinum metals are carried through the same procedure.

A method has been described for the determination of minute amounts of palladium in uranium compounds. Palladium, as well as gold and silver, is extracted from an acid solution by means of a chloroform solution of dithizone, the extract being evaporated and examined spectrographically.⁶

Another method⁸ separates palladium, platinum, and rhodium, after treatment of an acid solution with stannous chloride, by extraction with ethyl acetate. The extract is examined colorimetrically or spectrographically.

2. OSMIUM

The method for the determination of osmium was based on the separation of osmium from an acid peroxide solution as OsO_4 by distillation and on colorimetric determination by the use of thiourea.^{4,7} This method has also been investigated,^{9,10,12} and recoveries of not less than 70 per cent have been obtained on ranges of 10 to 70 γ .

Procedure for the Determination of Osmium in Uranium Metal and Oxides.⁷ In the determination of black oxide (U_3O_8), orange oxide (UO_3), brown oxide (UO_2), and peroxide ($UO_4 \cdot 2H_2O$) the apparatus used is a Scherrer arsenic still¹¹ modified in such a manner that the flask is removable, being attached to the apparatus by means of ground-glass joints.

Seventy-five milliliters of hydrochloric acid (1 to 1) is placed in a 100-ml graduated cylinder, which is used as the receiver, and is saturated with sulfur dioxide gas. The receiver should be kept in place, and a current of sulfur dioxide should pass through the solution during the entire procedure. If the sample is metal or peroxide, it is treated as follows: The 2.50-g sample is transferred to the reaction flask, the flask is placed in position, and the sample is dissolved with 30 ml of hydrochloric acid (1 to 2) added through the thistle tube. If necessary, the flask is warmed slightly to start the reaction. When solution is complete (usually in 5 to 10 min), 2 ml of 30 per cent hydrogen peroxide in 10 ml of water is added. Gentle heating and slight agitation with the air current may be needed to speed the oxidation.

If the sample is brown, black, or orange oxide, it is treated as follows: A 2.5-g sample is washed into the reaction flask with a little water, and the flask is adjusted into position. Ten milliliters of hydrochloric acid is added through the thistle tube, followed by 5 ml of 30 per cent hydrogen peroxide. The sample is warmed slightly (strong heating destroys hydrogen peroxide before the oxide is in solution). Five milliliters of peroxide is usually enough to dissolve the sample, but more may be added if necessary. As soon as the solution is completely oxidized (becoming yellow in color), a current of air is passed through the system, and the solution is gently distilled for 30 min. The distillate-sulfite solution is transferred from the receiver to a 150-ml beaker, a few crystals of sodium chloride are added, and the solution is evaporated to dryness on a steam bath. The dry residue is moistened with 5 ml of hydrochloric acid (1 to 1), 1 ml of saturated thiourea solution is added, the beaker is covered, and the contents are heated to boiling for a few minutes (or until the pink color is developed) and then placed on the steam bath for 30 min. After cooling, the contents of the beaker are transferred to a 50-ml Nessler tube and made up to the 50-ml mark with distilled water. A pink color denotes osmium. The intensities of the pink color are compared with standards prepared by adding known amounts of osmium (from a solution containing 0.980 mg of osmium per milliliter in 2N HCl) to the reaction flask, along with 2.5 g of osmium-free sample, and carrying out the procedure as outlined above. Photometric determinations can be made.

Fifty micrograms of osmium can be readily distilled and determined by this method. This amount, which corresponds to 20 ppm in a 2.5-g sample, was sensitive enough for the material in question. Ruthenium does not interfere under the above conditions. The solution in the flask may be used for the separation of the remaining platinum group of metals for spectrographic analysis.⁴

3. RUTHENIUM

Ruthenium, like osmium, forms a volatile tetroxide, but it is more difficult to produce than osmium tetroxide. This characteristic forms the basis for the separation of ruthenium from osmium and the other platinum metals. When strong oxidizing agents such as sodium bromate or potassium permanganate are present, ruthenium tetroxide may be distilled from a nitric acid solution.^{9,13} Ruthenium is not volatilized when osmium is distilled in the absence of a strong oxidizing agent.

In the analysis of ruthenium-uranium alloys in which ruthenium is present in small quantities (1 per cent), it is convenient to separate uranium as the peroxide and to precipitate metallic ruthenium from an acid solution with magnesium turnings.^{16,17}

Ruthenium may be determined colorimetrically by using thiourea, thiourea derivatives, thiocyanate, or 8-hydroxyquinoline.¹³

Recovery by means of distillation separation and colorimetric analysis with thiourea averaged more than 90 per cent.¹⁷ Other distillation experiments showed complete recovery of radioactive ruthenium in one recycling by the use of 6N sodium hydroxide as the receiving solution. Ethanol is used to precipitate the ruthenium oxides from the receiver solution.^{18,19}

Polarographic studies²⁰ of ruthenium in potassium chloride and pyridine solutions gave poorly formed waves that had the characteristic dip associated with platinum.

3.1 Gravimetric Determination. The following method, by Holt,¹⁷ was used for alloys containing approximately 1 per cent ruthenium in uranium: Uranium is oxidized to uranyl ion with peroxide and then removed by a peroxide precipitation. Ruthenium is precipitated as metal from hydrochloric acid solution by the addition of magnesium turnings. The ruthenium is filtered off, ignited, reduced in hydrogen, and weighed. Any other element of the platinum group interferes. If any elements of this group are present, the distillation separation may be used. The precision is ± 2 per cent in the range of 1 per cent ruthenium in uranium. The accuracy is ± 3 per cent for samples weighing 5 to 10 g.

Procedure. A 5-g sample is dissolved in concentrated hydrochloric acid, and hydrogen peroxide is added to oxidize all the uranium to uranyl ion. The excess peroxide is boiled off, the solution is filtered, and the filtrate is retained. The residue is washed with hot dilute hydrochloric acid and a little 5 per cent ammonium sulfate. The filter paper and residue are dried in a silver crucible, and the paper is burned off. The residue is fused with a mixture of sodium hydroxide and sodium peroxide (3 to 1). The melt is leached with water in a beaker, and the solution is made acid with hydrochloric acid. The solution is boiled, filtered, and washed with dilute hydrochloric acid; and the filtrate is combined with the first filtrate. The combined filtrate is made up to volume, and aliquots are taken containing approximately 0.1 g of ruthenium. The aliquots are diluted to 50 to 75 ml, 10 to 15 ml of 30 per cent hydrogen peroxide is added, and the solutions are centrifuged. The supernatant liquid is filtered. A few drops each of concentrated hydrochloric acid and hydrogen peroxide are added to the residue in the centrifuge cup, which is stirred, diluted to 50 ml, and centrifuged. This is repeated until all the wash solutions are colorless. The combined supernatant solutions are then boiled, and magnesium turnings are added slowly until all the ruthenium color disappears. The solution must be kept acid with hydrochloric acid during this process. The solution is boiled to coagulate the ruthenium precipitate and is then filtered, washed with hot water, hot 3N nitric acid, and 5 per cent ammonium sulfate. The precipitate is dried in an oven at 110°C. It is then heated in a weighed Rose crucible, and the carbon is burned off. The cover is put on, the stem is connected to a hydrogen tank, and the crucible is heated in a stream of hydrogen for about 15 min. The flame beneath the crucible is removed, and the crucible is allowed to cool in the hydrogen flame. The hydrogen flame is extinguished, and the crucible is further cooled in the stream of hydrogen gas. Finally the crucible is removed and cooled in a desiccator, and the ruthenium is weighed as the element.

3.2 Colorimetric Determination. The following procedure, by Williams,⁹ is used for traces of ruthenium in uranium metal and uranyl nitrate samples. A blue color is formed with ruthenium solutions on the addition of thiourea. The volatile tetroxide of ruthenium is distilled from the solution after osmium has been distilled off and after the remaining solution, containing ruthenium, has been strongly oxidized by potassium permanganate. If osmium is absent, the first distillation is unnecessary. If sodium bromate is used as the oxidizing agent, as it is in the analysis of macro amounts, enough free bromine is present in the distillate to interfere with the color. Potassium

permanganate has been found satisfactory as an oxidant. The method is sensitive to 5 γ in 5- to 15-g samples.

Procedure. After the sample has been dissolved in nitric acid, the solution, representing 5 g of uranium or 15 g of uranyl nitrate, is diluted to about 100 ml with water, and 5 g of potassium permanganate is added. The still is connected, and 10 ml of hydrochloric acid saturated with sulfur dioxide is put in the receiver. The flask is heated gently until the first rush of gases subsides. The flame is then adjusted so that practically nothing distills over for 20 min; then the flame is turned up so that a total of 15 ml is distilled over in the next 40 min, the whole distillation being completed in 1 hr. The total volume of the distillate is measured, and standards are prepared of the same volume containing 5 ml of hydrochloric acid saturated with sulfur dioxide; 0.5 ml of 10 per cent thiourea solution is added, and the tubes are heated in a boiling water bath for 5 min. The blue color is matched visually with the standards, and the ruthenium is determined.

4. RHODIUM

In one method⁸ used for the analysis of uranium metal and uranium oxide, a strong hydrochloric acid solution of the material is treated with stannous chloride and is then extracted with ethyl acetate. The extract is examined with a Lovibond tintometer, and a limit on the sum of the platinum and rhodium content is estimated. A spectrographic examination of the extract is made if the concentration of the two elements is over 4 ppm. Palladium may interfere, but osmium, iridium, and ruthenium will not.

Procedure. A 5.00-g sample of the metal is dissolved by adding 20 ml of water, followed by a mixture of 5 ml of hydrochloric acid and 5 ml of nitric acid. The amount of acid added is varied if the reaction is too vigorous or too slow. (Uranium oxide samples may be dissolved by adding 10 ml of nitric acid and warming.) The solution is evaporated to dryness, 20 ml of hydrochloric acid is added, and the solution is again evaporated to dryness. The residue is dissolved in 25 ml of water and 5 ml of hydrochloric acid, any siliceous insoluble matter being removed by filtration or centrifuging. Ten drops of stannous chloride (40 per cent in hydrochloric acid) are added to the solution. It is warmed to 90°C and cooled, and an additional 10 drops of stannous chloride are added, followed by extraction with 5 ml of ethyl acetate. The solution is run off and extracted with 5 ml more of ethyl acetate. The aqueous layer is run off, and the solvent is washed with 5 ml of sodium chloride solution containing 4 drops of stannous chloride solution. The wash liquor is run off, and the solvent layer is

filtered through a tiny plug of cotton. The extract is diluted to 3 ml, and its color is measured in a 1-cm cell in a Lovibond tintometer. If the color obtained is less than 1.0 yellow, the amount of platinum or rhodium present is less than 20 γ , i.e., less than 4 ppm. If the color obtained is more than 1.0 yellow, more than 20 γ of platinum or rhodium may be present, unless palladium has been detected previously. If the amount of platinum or rhodium present is more than 4 ppm, the concentration is determined by spectrographic methods.

5. PALLADIUM

The analysis for palladium consisted in the determination of traces in uranium compounds and uranium-bearing ores. Spectrographic examination of concentrates made either by the gold concentrate method⁴ or by the dithizone extraction method⁶ was employed for uranium compounds.

For traces in ores the following colorimetric method, employing *p*-nitrosodiphenylamine, has been used. Platinum(IV) does not react with this reagent, except in small amounts; it interferes, however, because of its color.

Procedure for Determination of Traces of Palladium in Ores.^{13,14}
The reagents used were as follows: Standard palladium solution, 0.001 per cent palladium in 1N hydrochloric acid, prepared by dissolving palladium metal in aqua regia and evaporating to dryness several times with hydrochloric acid; *p*-nitrosodiphenylamine, 5 mg dissolved in 50 ml of 95 per cent alcohol and diluted to 100 ml with water; sodium acetate-hydrochloric acid mixture, 240 ml of 1N hydrochloric acid and 200 ml of 1N sodium acetate diluted to 1 liter with water; stannous chloride, 20 per cent stannous chloride in 2N hydrochloric acid; tellurium solution, 62.5 mg of tellurium dioxide dissolved in 16.5 ml of warm hydrochloric acid and diluted to 100 ml with water.

The standards are prepared as follows: 1 ml of the standard palladium solution is diluted to 1 liter. Exactly 1-, 2-, 3-, 4-, and 5-ml portions of this solution are pipetted into 25-ml volumetric flasks. To each standard are added 50 mg of potassium pyrosulfate, 3 mg of potassium sulfate, 3 ml of sodium acetate-hydrochloric acid mixture, and 0.1 ml of the *p*-nitrosodiphenylamine reagent. Standards are made up to volume and thoroughly mixed. After standing for 1 to 2 hr the percentage of transmittancy of the solutions at 490 $m\mu$ is read against water.

Five-gram samples of the ores are weighed into 250-ml beakers. To each sample are added 25 ml of nitric acid and 80 ml of hydro-

chloric acid, the beakers are covered with watch glasses, and their contents are boiled down to about 30 ml. The sides of the beakers and watch glasses are washed down with water. The volume is brought up to approximately 150 ml with hydrochloric acid (1 to 1). The samples are filtered hot, and the filtrates are evaporated to dryness. This evaporation is repeated several times after the addition of hydrochloric acid (1 to 1). To the residues is added 25 ml of 2N hydrochloric acid. They are heated to boiling and then cooled. If lead chloride crystallizes out, the solutions are filtered. The solutions are diluted to about 50 ml with 2N hydrochloric acid. One milliliter of the tellurium solution (0.5 mg of Te) is added in the cold, and then 10 ml of 20 per cent stannous chloride is added dropwise with stirring. The solutions are boiled until the tellurium coagulates, allowed to stand for about an hour, and then filtered through a small porous-porcelain filter crucible (about 10 ml capacity), all the tellurium being transferred to the crucible. The tellurium is dissolved in a warm mixture of 0.5 ml of nitric acid and 1 ml of hydrochloric acid, allowed to stand in the crucible for a few minutes, and then collected with suction in a 5-ml porcelain crucible. The filter crucible is washed with 2 ml of hydrochloric acid (1 to 500) and again with 1 ml of the same. Three milligrams of potassium sulfate is added, and the solution is cautiously evaporated to dryness. The crucible is heated strongly over a Meker burner until all the tellurium has volatilized. After cooling, 1 drop of nitric acid and 3 drops of hydrochloric acid are added. The solution is evaporated to dryness, and the residue is taken up in a little dilute hydrochloric acid (1 to 500) and transferred to a 50-ml beaker. The remaining residue in the crucible is fused with 50 mg of potassium pyrosulfate and cooled, and 1 drop of nitric acid and 3 drops of hydrochloric acid are added. After evaporating to dryness, the remaining residue is taken up in a little dilute hydrochloric acid (1 to 500) and transferred to the 50-ml beaker. If cloudy, the solution is filtered through a small porous-porcelain filter crucible. Three milliliters of sodium acetate-hydrochloric acid mixture is added to the solution, which is then transferred to a 25-ml volumetric flask. A 0.1-ml amount of the *p*-nitrosodiphenylamine reagent is added, the solution is made to volume and mixed thoroughly, and after 1 to 2 hr the percentage of transmittancy is read at 490 m μ . The palladium concentration is determined by interpolating between the transmittancy reading of the standards.

6. IRIDIUM

The analysis of iridium has been made chiefly by separation and subsequent spectrographic examination of a concentrate.^{5,7,21} In an-

other method 1 mg of ferric iron is used to carry the iridium from the uranium solution upon the addition of sodium bicarbonate and ammonia.²¹ The solution is boiled to complete the precipitation of the iron. If the sample contains more than 1 mg of iron, it must be removed prior to the separation of the iridium. This is easily performed by removing iron as its cupferrate with a chloroform extraction. The limit of detection is 50 γ .

Traces of iridium in platinum or rhodium may be determined by beta activity excited by slow neutrons.²²

7. PLATINUM

The determination of platinum in trace quantities in uranium compounds has, in the majority of cases, been made by spectrographic means after concentrating with gold as a carrier.⁷ It has also been made on the concentrate obtained by means of stannous chloride, followed by ethyl acetate extraction.⁸ Gold and platinum in some uranium-bearing ores have been analyzed by concentrating these metals with tellurium as a carrier¹⁵ and examining the residues spectrographically. The platinum content of catalysts has been obtained by igniting to remove the organic matter, dissolving in aqua regia, and finally precipitating the platinum with hydrogen sulfide. The material analyzed did not contain other elements that would be precipitated by hydrogen sulfide.

7.1 Procedure for Separation of Platinum and Gold in Ores and Residues.¹⁵ The reagents used are stannous chloride (20 g of stannous chloride is dissolved in 17 ml of hydrochloric acid and diluted to 100 ml) and a tellurium solution (5.000 g of tellurium powder is dissolved in 15 ml of hydrochloric acid and 5 ml of nitric acid, evaporated to dryness, taken up in hydrochloric acid, evaporated to dryness three times, taken up in 2N hydrochloric acid, filtered through a tight Whatman No. 42 filter paper, and washed well with water, whereupon the filtrate is diluted to 500 ml with 2N hydrochloric acid, 10 ml of the final solution equaling 100 mg of tellurium).

A 1.0000-g sample is weighed into a 600-ml beaker. Then 350 ml of water and 10 ml of hydrochloric acid are added, and the solution is heated to boiling. Ten milliliters of 10 per cent sodium bromate solution is added, the sample is digested on the steam bath for 1 hr and heated to boiling, and 5 ml of 10 per cent sodium bromate solution is added. Sodium hydroxide solution (10 per cent) is added until a pH of 10 is obtained. The pH may be determined on a pH meter, or indicator paper may be used. The solution is boiled to coagulate the precipitate, and then it is filtered through a tight Whatman No. 42 filter paper, the precipitate being discarded.

Twenty milliliters of hydrochloric acid is added to the filtrate, which is evaporated to dryness on the steam bath. A little water is added, and the evaporation with hydrochloric acid is twice repeated. The residue is dissolved in 30 ml of hot 2N hydrochloric acid and filtered into a 150-ml beaker, with hot 2N hydrochloric acid washed in until the volume is approximately 50 ml. Ten milliliters of the tellurium solution, containing 100 mg of tellurium, is added. The tellurium is precipitated by adding slowly, with constant stirring, 10 ml of the stannous chloride solution. The precipitate is coagulated by heating and stirring. After standing overnight, the supernatant liquid is tested for complete precipitation with a little more stannous chloride solution. If no precipitate forms, the solution is filtered through a tared sintered-glass crucible of 30 ml capacity and fine porosity. The precipitate is washed several times with cold 2N hydrochloric acid, once with alcohol, and then with ether; it is next dried at 100°C for 1 hr, cooled, and weighed. The platinum content of the precipitate is determined by spectrographic means.

7.2 Procedure for Determination of Platinum in Carbon Catalyst.²³

The sample is ground until it passes through a 50-mesh sieve (a Braun grinder is used for this purpose). It is mixed thoroughly; 15 to 20 g is then weighed into a silica dish and placed overnight in an oven at 110°C. (This procedure seems to be necessary; otherwise, the material sprays when the water is given off at higher temperatures.) The sample is placed in a cold furnace, and the temperature is gradually increased to 600°C, the sample being allowed to burn slowly at this temperature overnight. The ignited sample is cooled and treated with 25 ml of dilute aqua regia (60 parts water, 40 parts hydrochloric acid, 10 parts nitric acid), heated on the steam bath for 3 to 4 hr to ensure the solution of the platinum, transferred to a 250-ml beaker with hot water, and evaporated to dryness on the steam bath. After cooling, the sample is treated with 10 ml of dilute hydrochloric acid (1 to 1), again evaporated to dryness, taken up with 20 ml of hydrochloric acid, diluted to 150 ml, digested on the steam bath for 30 min, filtered on a Whatman No. 42 filter paper, and washed with hot hydrochloric acid (1 to 99). The filtrate and washings are caught in a 600-ml beaker, diluted to 400 ml, and heated to boiling. The solution is then gassed with hydrogen sulfide for 1 hr by using a vigorous stream and keeping the solution near the boiling point. The solution is cooled somewhat by placing asbestos pads under the beakers on the hot plate. Gassing is continued for 15 min. After being allowed to stand overnight, the precipitate is filtered off on a Whatman No. 42 filter paper, washed with dilute hydrochloric acid (1 to 99), and ignited in porcelain to constant weight.

While this procedure does not remove the hydrogen sulfide metals, the results were the same as those obtained when the base metals were precipitated by the hydrolytic procedure proposed by Gilchrist.³ The residues were examined spectrographically, but only traces of copper and other acid sulfide metals were found.

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Chapter 22

SCANDIUM, YTTRIUM, AND THE RARE EARTHS

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Since the rare earths occur as fission products, considerable work on their separation and subsequent radiochemical determination was performed. The separation of the individual rare earths has had considerable emphasis, but it will not be considered in this chapter. Emphasis is placed here on methods of group separation rather than on the separation of individual elements. The determination of the individual rare earths has generally been made by spectrochemical means. Radiochemical methods of determination are considered in Volume 9, Division IV, of the National Nuclear Energy Series.

Scandium and yttrium are chemically very similar to the rare earths and, since they are usually separated with them, are discussed in this chapter.

The materials examined were essentially of a uranium or a thorium base, and the methods of solution are considered in Chap. 1 on "Uranium" and Chap. 2 on "Thorium."

1. METHODS OF SEPARATION

The methods of separation used depend on the nature of the constituents present. Since uranium is the most frequently encountered element in most of the materials under consideration, and since it interferes in the precipitation separations commonly used, the removal of uranium is an important preliminary separation. The separation from uranium may be accomplished by the extraction of uranyl nitrate by ether; by complexing the uranium either as salicylate or as peroxide, followed by hydroxide precipitation; by complexing the uranium as oxalate, with subsequent precipitation of the rare-earth oxalates; or by precipitation of the uranium as peroxide, with retention of the rare earths in solution.

Separation from thorium has been accomplished by the extraction of the salicylate complex of thorium as well as by the volatilization of thorium chloride.

After the removal of the bulk of interfering elements, precipitation as hydroxide, fluoride, oxalate, or, in the case of cerium, iodate may be employed. Ion-exchange methods have been used to separate the individual rare-earth elements,^{1,2} but they have not been employed for analytical purposes.

1.1 Precipitation. Of the various reagents that can be used to precipitate the rare earths, oxalic acid, hydrofluoric acid, and sodium or ammonium hydroxide have been employed to the greatest extent.

(a) Oxalate Precipitation. Oxalic acid is generally the most useful precipitation reagent for the rare-earth elements, because the separation from other elements is good and the oxalate precipitate can be readily ignited to the oxide. This method of separation has been extensively used both for the separation and for the determination of mixed rare earths.⁵⁻⁸ Ammonium oxalate has been used for the precipitation of the rare-earth oxalates,³ but this method is not to be recommended, since some of the yttrium group of elements (Y, Dy, Ho, Er, Tm, Yb, Lu) are soluble to some extent in this reagent. Scandium and thorium oxalates are also soluble in an ammonium oxalate solution. The rare-earth oxalates are soluble to some extent even in the presence of excess oxalic acid, and the smallest volume possible for precipitation is used. Excess mineral acid is to be avoided, since the solubility is increased. Figure 22.1, taken from Sarver and Brinton,³³ shows this effect as applied to the oxalates of the lanthanum group.

In the presence of large amounts of uranium the rare-earth oxalates are not completely precipitated unless sufficient oxalate ion is present to complex all the uranium.⁴ Ferric ion exhibits an effect similar to uranium.¹³ In the determination of traces of rare earths in large amounts of uranium it is practically impossible to separate the rare earths completely by an oxalate precipitation. Separations from the common elements are made, but not from thorium, yttrium, scandium, or actinium. Calcium is separated by a hydroxide precipitation in the presence of ammonium salts.

The following procedure has been used for milligram quantities of rare earths:

Procedure. A hydrochloric acid solution containing 0.3 to 10 mg of mixed rare-earth oxides is evaporated just to dryness in a 50-ml beaker. The residue is treated with 5 ml of a saturated solution of oxalic acid and 20 ml of water and is digested at 90°C for 10 min. The digestion is continued at room temperature for several hours or

overnight. The rare-earth oxalates are filtered on a small ashless paper of high retentivity and are washed with 0.5 per cent oxalic acid solution. The precipitate is ignited in a weighed crucible, with the final ignition at 950°C or higher for 15 min. It is then cooled and weighed.

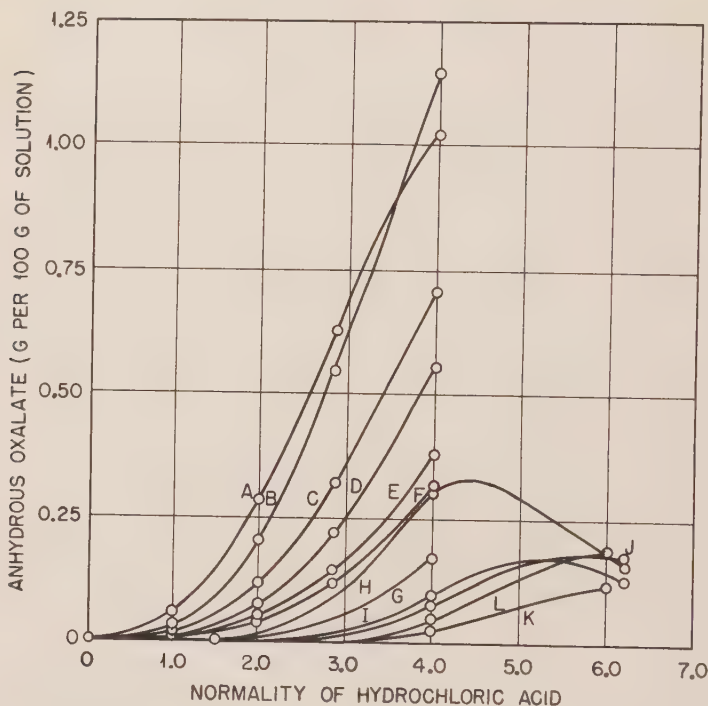


Fig. 22.1—Solubility of rare-earth oxalates in hydrochloric acid. Oxalic acid (0.1N): A, lanthanum oxalate; B, cerous oxalate; C, praseodymium oxalate; D, neodymium oxalate; E, samarium oxalate; F, gadolinium oxalate. Saturated oxalic acid: G, lanthanum oxalate; H, cerous oxalate; I, praseodymium oxalate; J, neodymium oxalate; K, samarium oxalate; L, gadolinium oxalate.

(b) Fluoride Precipitation. The precipitation of the rare earths as fluorides is one of the classic methods of separation,³ since titanium, zirconium, columbium, and tantalum are not precipitated. It has been especially useful in the separation of traces.^{5,9} Scandium is dissolved in the presence of ammonium fluoride, and this method has been used to separate it from the rare earths. In the presence of alkali fluorides the solubility of the rare-earth fluorides is increased.¹² Uranium appears to have a solvent effect upon the rare-earth fluorides. During the precipitation of microgram quantities, amounts that

could be quantitatively recovered from pure aqueous solutions were not recoverable in the presence of 10 to 20 g of uranium.⁹

Fluoride separation of rare-earth fission products has been employed extensively in conjunction with lanthanum, cerium, yttrium, and praseodymium as carriers prior to a radiochemical determination. The fluorides are readily soluble in a mixture of nitric acid and boric acid, and oxalates may be precipitated from this solution. By fuming with sulfuric acid the fluorides are converted to sulfates. Freshly precipitated fluorides are usually gelatinous in nature, thus making filtration slow and difficult. A long digestion period is generally necessary.

Procedure.⁹ The solution containing the rare earths is evaporated nearly to dryness in a platinum dish. It is diluted to 50 ml with water, 15 ml of 48 per cent HF is added, and the solution is stirred and allowed to stand for at least 3 hr, preferably overnight. The mixture is filtered through a Whatman No. 40 filter paper on a waxed funnel into a waxed beaker. The dish is washed with 20 ml of 5 per cent HF, and the liquid is used to wash the precipitate on the filter. The precipitate is finally washed once with water.

(c) Hydroxide Precipitation. The use of sodium or ammonium hydroxide as a precipitating agent for separation purposes is of little value. So many other elements are precipitated that hydroxide separations are chiefly useful in separating the rare earths from the alkalis and the alkaline earths. The method has been used in conjunction with other separation processes, particularly with the fluoride and oxalate methods. For complete precipitation, especially in the presence of lanthanum, the pH of the solution should be high. Ammonium hydroxide in an excess of 10 per cent is necessary with ammonium salts present. Sodium hydroxide has been used with sodium peroxide to separate the rare earths in the presence of large amounts of uranium.⁶ Hexamine has been used to separate thorium from the rare earths (Chap. 2, "Thorium").¹⁸ Ammonium hydroxide has been used to separate the rare earths from small amounts of uranium after complexing the uranium with salicylic acid.⁹ The solubility of the rare-earth hydroxides is considerably increased, however, in the presence of salicylic acid.

Procedure. A hydrochloric acid solution of the mixed rare earths is diluted to 200 ml, and 10 g of NH_4Cl is added. The solution is neutralized with NH_4OH (sp. gr. 0.9), and then 10 per cent by volume is added in excess. The precipitate is digested at 90°C for 15 min, cooled, and filtered at room temperature on a paper of medium retentivity. The hydroxides are washed with a solution of NH_4OH (1 to 9) containing 5 per cent ammonium chloride.

(d) Other Methods. Several other methods of separation applicable to individual rare-earth separations have been used chiefly for radiochemical analysis. The precipitation of cerium as ceric iodate was suggested by Brinton and James¹⁴ and employed¹⁵ for the determination of cerium activity from fission products. The potassium carbonate separation method of Meyer and Muller¹⁶ was used for the separation of yttrium from lanthanum.¹⁷ The separation of yttrium from lanthanum was found to be 90 to 95 per cent effective when the precipitate formed was in a crystalline state. Scandium has been separated as the hydroxide after complexing uranium with sodium carbonate and hydrogen peroxide.^{19,20}

(e) Peroxide Precipitation of Uranium. The separation of the bulk of the uranium by precipitation as the peroxide has been employed prior to a rare-earth determination.^{8,21} By precipitating at a pH of about 1 and using radioactive rare-earth tracers it was found that less than 1 per cent of the rare earths is retained in the peroxide precipitate.²¹ A gravimetric study of the optimum pH for this peroxide separation was also made.³⁵ In the presence of appreciable amounts of iron (3 g in 50 g of UO_3) less consistent results were obtained. In one instance, in which 5.1 mg of samarium oxide was added, 4.7 mg was recovered.⁸

Procedure.²¹ Crude sodium uranate is redissolved in HCl, the solution obtained is filtered and diluted to about 10 per cent in uranium, the pH is adjusted to 1.5, and the solution is cooled to 25°C. Then 120 per cent of the theoretical amount of 30 per cent H_2O_2 is added with constant stirring, and the precipitate is allowed to settle. The precipitate is then filtered or centrifuged and is very thoroughly washed with 0.01N acid solution and finally with distilled water. The rare earths are separated from the solution by the fluoride or oxalate method.

(f) Carriers. Various carriers for traces of rare-earth elements have been used. Although their chief use has been in radiochemical work with fission products, some application has been found for trace determinations of rare earths in uranium and its salts. Lanthanum, cerium, praseodymium, and yttrium have been used chiefly in the form of fluoride for the isolation of fission products.^{10,11} Yttrium, iron, and copper²² have been used as carriers for the isolation of rare earths prior to spectrochemical determination.

(g) Complex Formation (Uranium). Uranium in an alkaline peroxide solution forms a soluble peroxy complex that has been used extensively as a means of separating the rare earths from relatively large amounts of uranium. The separation can be made in solutions having a very high pH.⁷ Alkali carbonates form complexes with uranium,

and rare-earth carbonates, especially of the yttrium group, are also dissolved to some extent. The procedure is given below in the section on selected procedures.

1.2 Extraction. Separation of the rare earths from uranium and thorium by extraction has consisted of extracting the bulk of the uranium as the nitrate by ether and extracting thorium as the salicylate.

(a) Ether Extraction. The ether extraction of uranium prior to a rare-earth determination has been known for several years (see references 5, 7, 8, 9, 22). The procedure is different from the method described in Chap. 1 on "Uranium," because the conditions should be such that not all the uranium is extracted. If salting agents are used, the possibility exists of some rare-earth material being extracted. If the amount of uranium is 50 mg or less, an ether extraction is not necessary.

Procedure.⁷ A 50-g sample of U_3O_8 is dissolved in 75 ml of HNO_3 (1 to 1) by heating on a steam bath. The solution is evaporated to dryness; then, after cooling, the crystals are dissolved in 100 ml of ether and 5 ml of H_2O or dilute HNO_3 (1 to 4),³⁶ with stirring and swirling until solution is complete. The ethereal solution is transferred to a separatory funnel, and the residue in the beaker is rinsed into the funnel with 3- to 5-ml portions of ether. The funnel is stoppered and shaken vigorously for 30 to 60 sec. The liquid is allowed to stand for a few minutes, and any water that is separated out is drained into the original beaker. Five milliliters of water is added to the funnel; the mixture is again shaken and then allowed to settle. The water layer is drained into the beaker. The extraction is repeated with another 5-ml portion of water, and the water layers are combined.

(b) Salicylate Extraction. For the isolation of rare earths from thorium the extraction of thorium salicylate in an ammonium nitrate-acetic acid mixture by means of a mixture of 90 per cent ethyl acetate and 10 per cent ethyl ether has been suggested. The method was not tested for less than microgram quantities of rare earths.

1.3 Volatilization. The rare earths in thorium²³ and uranium have been separated by volatilization of the chlorides in a stream of sulfur chloride. The separation of rare earths by this method has been suggested by several workers.^{24,25} Microgram amounts of rare earths were separated in this manner from large amounts (10 g) of uranium with slight loss. Porcelain boats were found unsatisfactory for holding the samples. The distillation must be performed slowly and carefully; otherwise, mechanical loss of the rare earths occurs.

Procedure.²³ A 1-g sample of thorium nitrate containing the rare earths is weighed into a silica boat (8 by 1 by 1 cm). If only trace

amounts of the rare earths are present, 1 ml of a solution of yttrium chloride containing 1 mg of yttrium is added to the boat as a carrier, and the solution is slowly evaporated in an oven. Since thorium nitrate has a tendency to swell, it is pressed into the boat with a porcelain spatula from time to time. After the water has completely evaporated, the nitrate is decomposed to the oxide by careful heating. The boat is then placed in a silica tube and heated to about 650°C in a cylindrical combustion furnace. Sulfur monochloride is placed in a 250-ml short-necked distilling flask fitted with a 35/20 ball joint sealed to a short length of pyrex tubing, which is bent at a right angle and constricted in order to make a loose fit with the silica tube. Several layers of glass tape are wrapped around the pyrex tube, which is then inserted into the silica tube. More tape is wrapped on the outside and held in place by adhesive tape. The connecting tube is lagged with asbestos. The distilling flask is heated electrically to provide a slow stream of sulfur chloride vapor and chlorine into the silica tube. The thorium chloride produced by the reaction collects in the colder part of the tube. The contents of the boat are treated with sulfur chloride until all the thorium is removed. The boat is cooled, and the residue is dissolved in hot hydrochloric acid.

2. METHODS OF DETERMINATION

The oxalate procedure was used for the analysis of macro amounts of rare earths, followed by the spectrophotometric determination of some of the individual rare earths.^{2,26,29} The total rare earths were obtained either as the oxalate or as the hydroxide. They were then ignited to the oxide and weighed. The mixed oxides were then examined by spectrographic means. In several cases the hydroxide precipitates were dissolved in HCl, and this solution was used for spectrographic analysis. Although fluorescent methods were suggested for the determination of the rare earths, they were not employed.

2.1 Gravimetric Methods. The gravimetric determination of the rare earths involved their precipitation as the oxalate or the hydroxide, followed by ignition and the weighing of the oxide. The procedures for these precipitations have been given above in the section on methods of separation, but, since they are useless as determinations without previous separation, the complete procedures for gravimetric determinations are more adequately covered in the selected procedures given later in this chapter.

2.2 Spectrophotometric Methods. Many of the rare earths show characteristic absorption spectra. Use has been made of this phenomenon to determine individual rare earths in mixtures. Although the visible region has bands³⁴ that may be used for several of the ele-

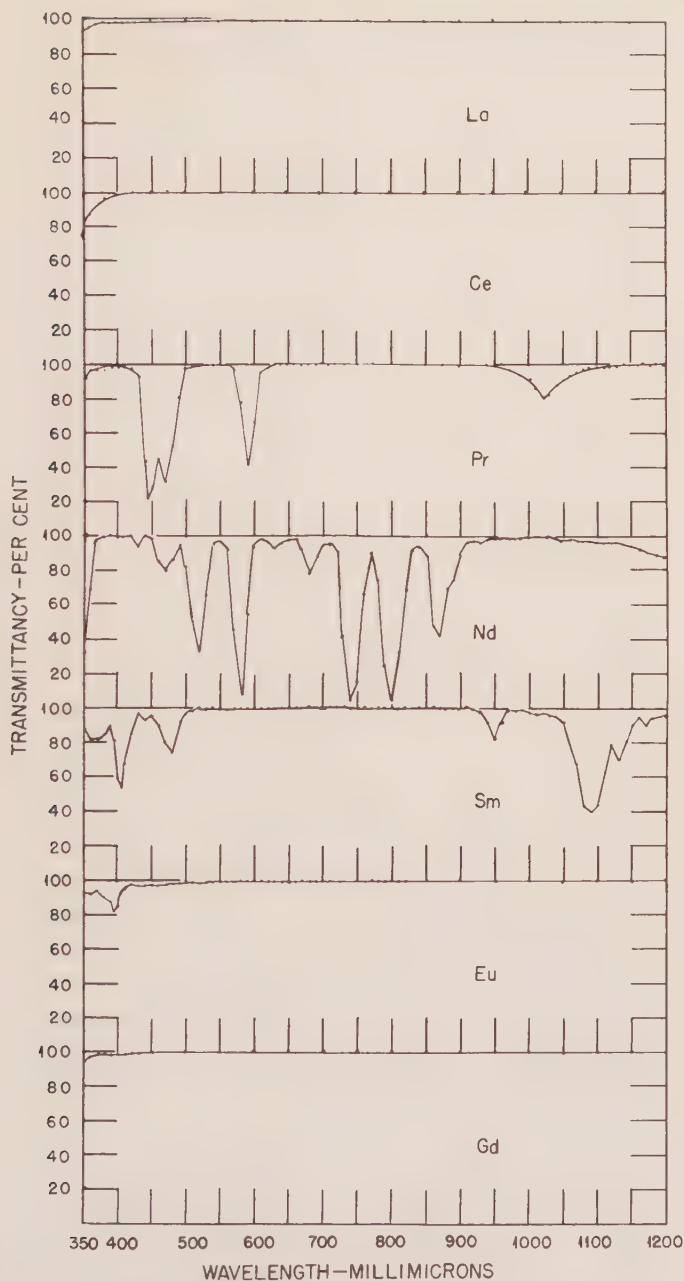


Fig. 22.2 — Spectral transmittancies of rare-earth nitrate solutions.

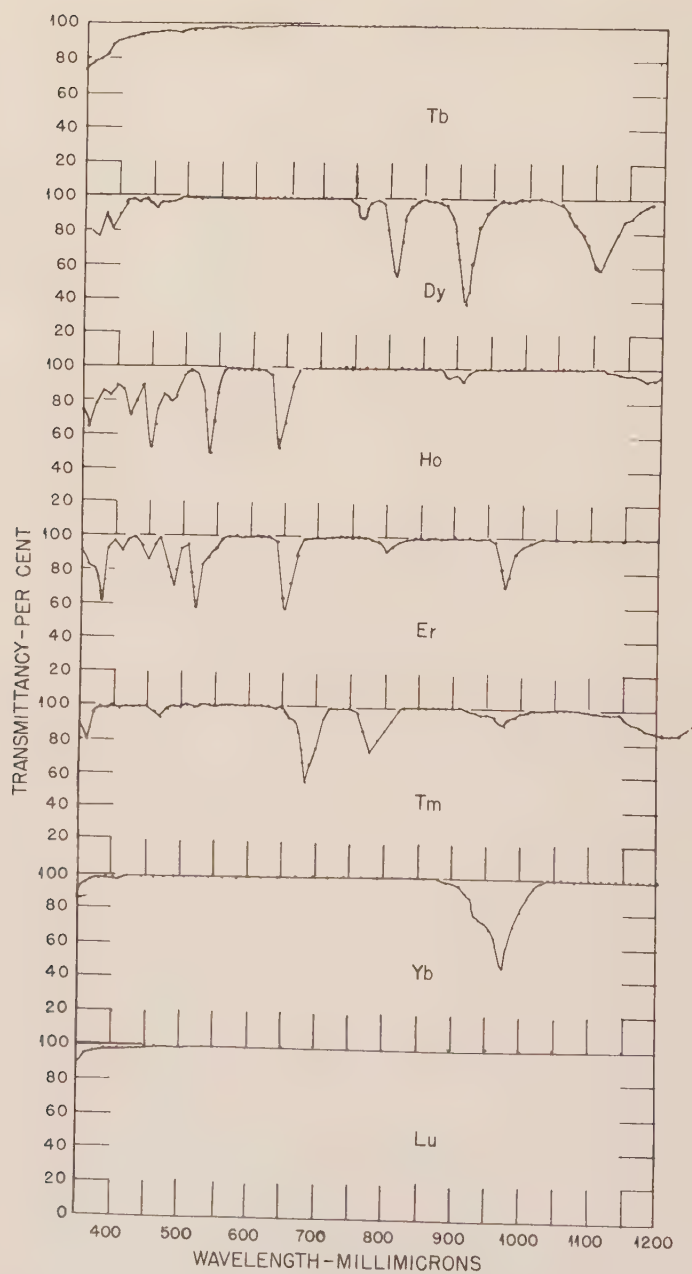


Fig. 22.3—Spectral transmittancies of rare-earth nitrate solutions.

ments, the most characteristic bands for other elements are in the infrared portion of the spectrum. Ytterbium does not exhibit bands in the visible region, but does in the infrared. Also, the most characteristic bands for samarium and dysprosium are in the visible region. Figures 22.2 and 22.3 show the spectral transmittancies of rare-earth

Table 22.1—Wavelengths of Rare-earth Absorption Bands

Element	Wavelength, $m\mu$	Element	Wavelength, $m\mu$
Praseodymium	446	Holmium	452
			539
Neodymium	521		643
	798	Erbium	489
			521
Samarium	402		653
	1088		976
Dysprosium	808	Thulium	684
	910		780
	1102	Ytterbium	973

nitrate solutions.²⁶⁻²⁸ Table 22.1 gives the wavelength of the characteristic absorption bands of various elements that can be used for analysis.

The spectrographic determination of the individual rare-earth elements present in rare-earth concentrates, obtained by a combination of the above separation methods, was employed to a considerable extent (see references 9, 22, 30, 31). In several instances the solution of the rare earths was evaporated on copper⁹ or carbon electrodes and then arced. Iron,²² copper,²² and yttrium have been used as carriers. Molybdenum³² and titanium³⁰ have been used as internal standards because of the nonreproducibility of the matrix. Table 22.2 gives the spectral lines used in the various methods of analysis. It is interesting to note that in very few instances are the recommended lines the same.

3. SELECTED PROCEDURES

The following procedures, illustrating the above separations, are typical of those used in the analysis of Project materials.

3.1 Ether-extraction Spectrographic Method.⁹ Ten grams of U_3O_8 is dissolved in HNO_3 (1 to 1). If solution is not complete, the residue is filtered off, washed, ignited, and finally fused with 0.5 to 1 g of potassium bisulfate in a platinum crucible. The melt is dissolved in

Table 22.2—Spectral Lines of Rare-earth Elements

Element	Wavelength, angstroms				Limits,* ppm
	British	Canadian	National Bureau of Standards	Massachusetts Institute of Technology	
Yttrium	3600.73 3710.29 3788.70 4374.94			3327.88 4374.94 3242.28	<0.1
Europium	4594.02 4627.12 4661.88	2906.67 G 3907.11 F 3972.0 G 4594.02 F	3907.11 3971.99	4594.02	0.02
Gadolinium	3345.99 3350.10 3362.24	3010.14 F 3032.85 F 3034.0 G 3100.5 G 3422.47 G	3422.47	3358.63	0.04
Samarium	3568.26 3592.59 3634.27	3260.3 G 4424.34 F 4434.32 F	3306.37	4334.15 4434.32	0.3
Dysprosium	3407.80 3531.71 3645.42 4000.45 4211.72		3385.03 3407.80	4308.62 3968.40	0.04
Erbium			3264.78		0.04
Cerium			4012.39 4040.76		<0.1
Holmium			3416.46 3398.98		0.04
Lanthanum			3988.52 3265.67		<0.1
Lutecium			2911.39 2900.30		<0.5
Neodymium			3951.15 3963.11		<0.5
Praseodymium			4008.71		<0.5
Scandium			3353.73 3613.81		<0.1
Terbium			3324.40		1.0
Thorium			2870.41 4019.14		1.0
Thulium			3131.26 3151.04		0.04
Ytterbium			3289.37		0.004

*Set by National Bureau of Standards.³⁰

HCl, and as much of the acid as possible is evaporated off on a steam bath. This solution is transferred to a platinum dish, and the rare earths are precipitated with HF, as described below for the main solution. This fraction is carried through the determination, as described for the main portion, and any rare earths found are added to the result for the main solution.

The main solution is evaporated until crystallization of the uranium nitrate just commences; then, after cooling, any lumps are broken up with a glass rod. If the cooled material is not broken up, it sets in a crystalline mass that is difficult to dissolve in ether. The crystals are dissolved in 70 ml of ether. The solution is poured into a separatory funnel, any insoluble matter being retained in the beaker as long as possible. The beaker is rinsed out with 10 ml of ether, which is added to the solution in the funnel. Sufficient water is added to give an aqueous layer of about 1 ml after shaking and separating. The funnel is shaken thoroughly, and the aqueous layer is run into the beaker containing the insoluble matter. The extraction is repeated with 1 ml of water, and this extract is added to the beaker. The ether layer is rejected, and the ether from the aqueous solution in the beaker is evaporated off at a low temperature. A small amount of water and 2 drops of HNO_3 are added to the residue. When the solution has evaporated almost to dryness, it is transferred to a platinum dish and diluted to 50 ml with water. Fifteen milliliters of 40 per cent HF is added and, after stirring, is allowed to stand for at least 3 hr, preferably overnight. The solution is filtered through a Whatman No. 40 filter paper on a waxed funnel and into a waxed beaker. The dish is washed out with 20 ml of 5 per cent HF, and the liquid is used to wash the precipitate on the filter. The precipitate is washed once with water and is then ignited in a platinum crucible. The dish is washed out with 1 to 2 ml of hot concentrated H_2SO_4 , care being taken that the hot acid comes into contact with the sides of the dish. This acid is added to the ignited precipitate in the platinum crucible, and the sulfuric acid is evaporated off to expel fluorine. The sulfated residue is dissolved in HCl (1 to 9) and evaporated almost to dryness in order to remove most of the acid. The solution is then transferred to a 50-ml beaker. The volume at this point should be 5 to 10 ml. One-tenth of a gram of salicylic acid is added, followed by excess ammonia. The solution is then stirred well and filtered through a Whatman No. 40 filter paper. This procedure requires about 5 min for an appreciable amount of precipitate, but for minimum amounts a 20- to 30-min precipitation period should be allowed. The precipitated hydroxides are washed with 5 per cent ammonia, and the beaker is rinsed out with water, which is run through the filter. The precipi-

tate is ignited and dissolved in a small amount of the HCl used to wash out the beaker in which the ammonia precipitation was made. The solution is transferred to a small beaker and evaporated to minimum volume.

This solution, containing the rare earths, is evaporated off on a depression in a 5-mm pure copper rod, which is made the lower (negative) electrode, of a 5-amp arc at 40 to 50 volts d.c. The upper electrode is a similar rod sharpened to a blunt pyramidal cone. A large Littrow spectrograph is used to make the analysis. The amounts of individual rare earths are estimated by comparison with standard plates.

3.2 Sodium Peroxide-Ammonium Hydroxide-Oxalate Method.⁶ A 20-g sample (proportionately smaller if a rare-earth content greater than 0.5 per cent is anticipated) is dissolved in 30 ml of dilute nitric acid (1 to 1). If considerable iron is present, as evidenced by an insoluble reddish-brown residue, 25 ml of hydrochloric acid is added (sp. gr. 1.18), and the solution is evaporated to a sirupy consistency. The sirup is dissolved in a small amount of dilute hydrochloric acid (sp. gr. 1.10) and cooled, and the acid solution is extracted in a separatory funnel with an equal volume of diethyl ether. The ether layer is washed with two small portions of dilute hydrochloric acid (sp. gr. 1.10), and the washings are combined with the solution of the sample. The ether that is dissolved in the solution is volatilized, and evaporation is continued to a volume of about 25 ml. The solution is cooled and diluted to 200 ml.

Thirty grams of sodium peroxide is dissolved in 600 ml of water, and a little paper pulp is added. Into this mixture the solution of sample is poured slowly, at the same time being stirred constantly but not too vigorously. The uranium, which may be precipitated momentarily, should be completely redissolved. The solution is filtered with gentle suction on a Buechner funnel; a hardened filter paper of medium retentivity (for example, Whatman No. 52) is used, on which a thin mat of paper pulp has been placed. The precipitate is washed well with a solution containing 0.5 per cent carbonate-free sodium hydroxide and 0.5 per cent hydrogen peroxide.

The hydroxide precipitate is dissolved through the filter with dilute hydrochloric acid (1 to 1), and the filter is washed well with water. The solution is diluted to 200 ml, and 10 g of ammonium chloride is added. The solution is neutralized with ammonium hydroxide (sp. gr. 0.9), and an excess of 10 per cent by volume is added. The precipitate is digested at 90°C for 15 min, cooled, and filtered at room temperature on a paper of medium retentivity. The hydroxides

are washed with a solution containing 10 per cent by volume of ammonium hydroxide (sp. gr. 0.9) and 5 per cent by volume of ammonium chloride.

The precipitate is dissolved with dilute hydrochloric acid (1 to 1), and the solution is evaporated to dryness. The residue is baked for several hours at 90 to 100°C. The residue is taken up in dilute sulfuric acid (1 to 99), and the solution is saturated with hydrogen sulfide gas. The solution is filtered through a paper of high retentivity and washed with water. The precipitate, which consists of heavy metal sulfides, silica, and barium, strontium, and calcium sulfates, is rejected.

The solution is boiled, any sulfides or sulfur that may have precipitated are filtered off, and a few drops of nitric acid are added to the hot solution to oxidize traces of iron, vanadium, etc., which were reduced by hydrogen sulfide. The volume is adjusted to 75 ml, and the rare-earth hydroxides are precipitated with ammonium hydroxide, as previously described.

The filtered and washed hydroxides are dissolved with dilute hydrochloric acid (1 to 1), and the solution is evaporated just to dryness. The residue is treated with 5 ml of a saturated solution of oxalic acid and 20 ml of water and digested at 90°C for 10 min; the digestion is continued at room temperature for several hours or overnight. The rare-earth oxalates are filtered on a small ashless paper of high retentivity and washed with 0.5 per cent oxalic acid solution. The precipitate is ignited in a weighed crucible with final ignition at 950°C or higher for 15 min. The precipitate is then cooled and weighed.

4. SPECTROGRAPHIC ANALYSIS OF THE CONCENTRATES

Addition of the Internal Standard (Titanium).³⁰ To prepare the rare-earth concentrate for spectrography the precipitate is dissolved in nitric acid (2 ml of 1 to 1 nitric acid per 10 mg of concentrate). A measured volume of standardized Ti solution such that the titanium is 1 per cent of the weight of the concentrate is added. The titanium solution, containing 0.1 mg of titanium per milliliter, is prepared by dissolving a National Bureau of Standards No. 154 standard sample of TiO_2 in H_2SO_4 , as described in the provisional certificate. The solution is evaporated on a steam bath to a volume of 0.5 ml, and two or three small circles of soft filter paper (cut with a No. 10 cork borer) are added and evaporated to dryness. The concentrate is ignited over a Meker burner slowly to avoid spattering.

The residue is then examined spectrographically, using the titanium line at 3361.22 for the internal standard.

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Part II

SPECIAL ANALYTICAL LABORATORY EQUIPMENT
AND TECHNIQUES

Chapter 23

ELECTROLYTIC SEPARATION METHODS

By C. C. Casto

Electrolytic methods for separating cations were widely used on the Project. Considerable development work was done on mercury-cathode electrolysis in acid solution. Although some of this work has been antedated by material published earlier, it is summarized nevertheless in this chapter.

1. MERCURY-CATHODE ELECTROLYSIS

In general, metals below manganese in the electromotive series can be made to deposit quantitatively in a mercury cathode. Uranium remains quantitatively in the electrolyte.¹⁻³ This means of separating certain metals in the form of amalgams was described by Gibbs^{4,5} and by Kollock and Smith.^{6,7} The application of mercury-cathode electrolysis in the determination of aluminum,⁸ boron,⁹ uranium,¹⁰ and vanadium¹¹ has been reported, and Pavlish and Sullivan¹² have presented considerable information on the effect of varying conditions in the mercury-cathode electrolysis.

Mercury-cathode electrolysis has been used to separate samples containing uranium and electrolyzable impurities. It was also employed as a step in the concentration of these impurities prior to volatilization of the mercury and the polarographic determination of impurities in the residue.

1.1 Use of Mercury Cathode for Purification of Uranium Solutions. Early workers carried out electrolyses in ordinary beakers (which were immersed in a cooling bath), using a layer of mercury as the cathode and a platinum anode. Later, a stopcock was added so that the mercury and the electrolyte could be drained from the cell. The specially designed electrolysis cell¹⁵ shown in Fig. 23.1 is one of the types used for the purification of uranium solutions. It is constructed

of glass tubing of large diameter and is provided with a water jacket for the circulation of cooling water.¹⁵ It is a modification of cells

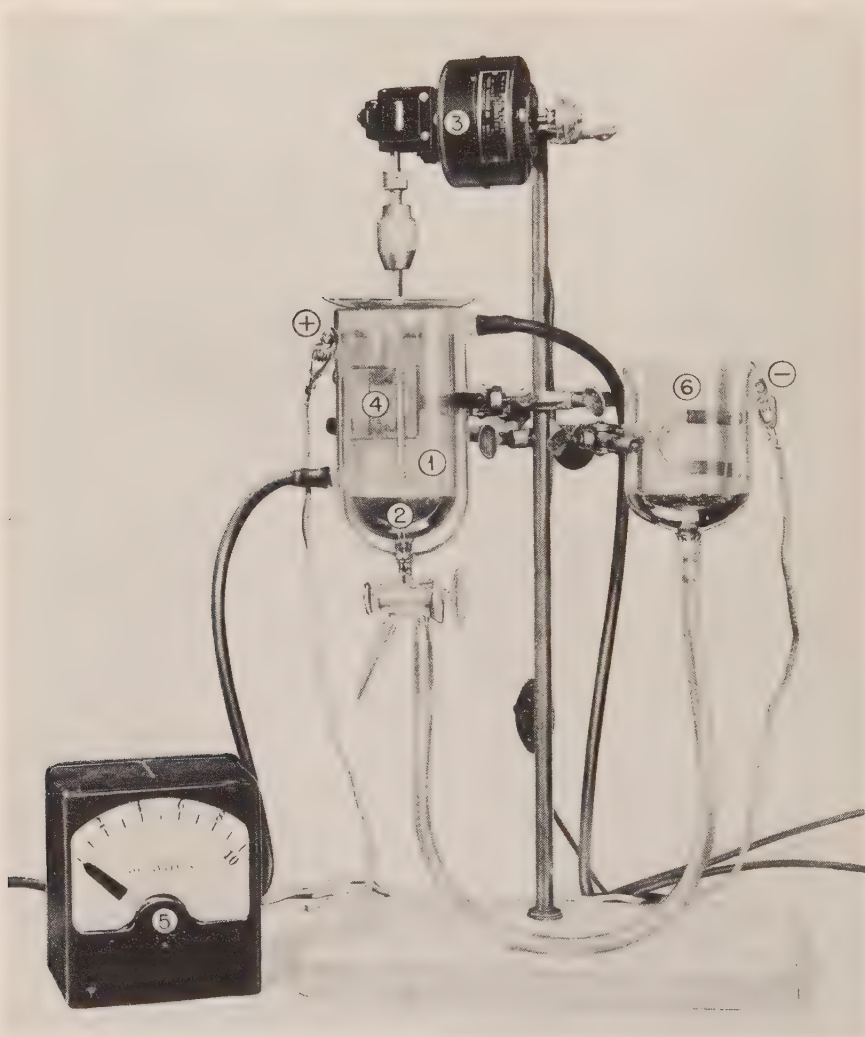


Fig. 23.1—Mercury-cathode electrolysis cell. 1, glass electrolysis cell; 2, mercury cathode; 3, stirrer; 4, platinum anode; 5, ammeter; 6, mercury-leveling bulb.

previously described by Melaven¹³ and Bennett,¹⁰ who used the cell for the separation of iron from uranium. A variation of this design, in

which the mercury-leveling bulb is replaced by a vertical tubular side arm connected to the cell through a three-way stopcock, is more compact than the design pictured here and has also been extensively employed.¹⁵

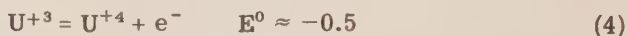
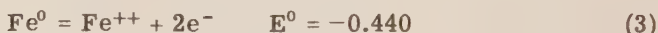
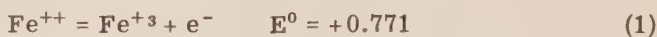
Some workers^{16,17} undertook a study to find the optimum conditions for the electrolytic removal of iron and chromium from uranium-bearing solutions. The expression "optimum conditions" will be mentioned frequently in the subsequent discussion of mercury-cathode electrolysis. This term, whenever used, will refer to the following conditions: current, 5.0 amp; voltage, sufficient to produce this current; acidity, 1.0N; electrolyte volume, 50 ml; anode, flat platinum spiral; cathode area, 21 sq cm; type of stirring, cathode only; uranium content, 0.25 g.

Project electrolyses have usually been performed in sulfuric acid mediums, but perchloric acid has also been used, as well as hydrochloric acid solutions with a 10 per cent iridium-platinum anode.¹⁵

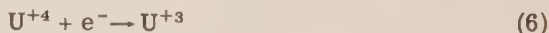
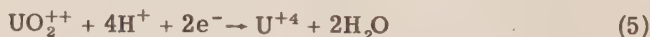
Furman and McDuffie¹⁴ have used a diaphragm electrolysis cell, in which impurities are electrolyzed out of the mercury cathode as rapidly as they are deposited therein. This function is accomplished by means of a two-compartment cell similar to the one described by Smith,⁷ the bottom of both compartments being the same mercury pool. One compartment contains the acidic sample solution and employs the mercury electrode as the cathode. The other compartment contains a dilute acid solution, in which the mercury electrode acts as the anode. The acid, preferably perchloric, used in the latter compartment should be one that does not form an insoluble salt with mercury(I) ion unless an oxidation-reduction buffer is present to prevent the oxidation of mercury at the mercury anode. Furman and McDuffie suggested using the iron (II)/(III) system [or the tin (II)/(IV) system] for this purpose. In operation, the impurities are deposited in the mercury cathode of the first compartment, containing the sample, and are then transported, by stirring the mercury, to the second compartment, where they are removed from the mercury anode. Those metals which are more easily oxidized than mercury will be dissolved from the impure mercury in preference to the oxidation of the mercury.

(a) Electrolysis from Sulfuric Acid Mediums. The electrolytic reduction of a sulfuric acid solution of a mixture of uranyl sulfate and ferric sulfate results first in a change of color from yellow to green as the uranium(VI) and iron(III) ions are reduced to the quadrivalent and the bivalent states, respectively. The deposition of bivalent iron then takes place, accompanied by the partial reduction of quadrivalent uranium to the red trivalent form. The oxidation-reduction potentials

for these reactions are given by Latimer.¹⁸ These potentials, with signs changed to conform with the European nomenclature used in this volume, are as follows:



The cathodic reduction of uranium in sulfuric acid solution proceeds according to the following equations:



The major anode reaction, occurring simultaneously with cathode reaction 5, is



and that with cathode reaction 6 is



It will be observed that 4 moles of hydrogen ion is required for the complete reduction of 1 mole of uranium(VI) ion to the quadrivalent state, but 2 moles of hydrogen ion is simultaneously produced at the anode by the oxidation of water. Obviously, if less than the requisite excess of 2 moles of hydrogen ion is initially present for each mole of uranium(VI) ion, the precipitation of the hydrated uranium(IV) oxide will occur.

Deposition Rate as Function of Acid Concentration. In the following sections the deposition rate is expressed either (1) indirectly, as the electrolysis time required to obtain a negative qualitative test for the element in the electrolyte, or (2) directly, as the average rate, or as the number of grams deposited divided by the total time required for complete deposition.

The findings of Pavlish and Sullivan,¹² which show that an increase in the concentration of free sulfuric acid increases the electrolysis time for iron, were confirmed.^{16,17} The same phenomenon was ob-

served for chromium, manganese, molybdenum, and nickel electrolyses in the presence of uranium, but not for copper and zinc electrolyses.

It was found^{16,17} that the times required for the complete reduction of iron(III) to iron(II) and of iron(II) to iron(0) were approximately doubled when the acidity was increased from 1.0N to 5.0N. This effect is illustrated in Fig. 23.2, where the reduction of iron(III) to iron(II) is shown to be markedly inhibited by increasing the acidity. This fact may be attributed to the anodic formation of perdisulfuric acid,¹⁹ with the consequent oxidation of iron(II) to iron(III).

The effect of acidity on the electrolytic deposition of chromium has been studied.⁷ With samples containing uranium, the magnitude of this effect is even greater than that of its influence upon iron deposition.^{16,17} When samples containing chromium(III) and uranium ions were electrolyzed under the same conditions as those used for the dilute iron solution, the deposition time increased approximately fourfold when the acidity was increased from 0.2N to 2N. At higher acidities chromium(VI) has been found in the electrolyte after the electrolysis of solutions that initially contained only chromium(III).

The effect of acidity on the deposition time was also studied for the elements copper, zinc, and nickel.^{16,17} Copper was shown to deposit at practically the same rate at all acidities between 0.1N and 6N. Zinc deposited at essentially the same rate for acidities no greater than 3N, but at 4N, the highest acidity tested, the rate decreased appreciably. The time for the deposition of nickel quadrupled as the acidity was increased from 0.1N to 3N.

The electrolytic removal of manganese was studied^{16,17} under conditions that were considered optimum for its deposition in the mercury cathode. Manganese was shown to be removed to the extent of 99.0 to 99.6 per cent after 1 hr of electrolysis; no further deposition seemed to take place when the electrolysis was continued for 2, 3, or 4 hr. As the acidity was increased, the removal became less complete, only 82.9 per cent being achieved after 1 hr of electrolysis in 6N acid, and 91.6 per cent being achieved after 2 hr at the same acidity.

Since molybdenum passes through several valence states in being reduced from molybdate ion to depositable metal, it would be expected to manifest properties similar to those of iron and chromium in having its deposition rate decreased by high acidities and consequently high persulfate ion contents. Only 13 per cent of the molybdenum was found to remain in the electrolyte after 1 hr of electrolysis in 0.3N H_2SO_4 , but the amount remaining increased continuously with increasing acidity, rising to 48 per cent at 3N acidity.

Deposition Rate as Function of Current. It is a known fact that, all other factors remaining constant, the rates of electrolytic deposition increase with increasing current. The actual magnitude of the increase in deposition rate was studied^{16,17} in 1N sulfuric acid with samples containing 1 g of iron and 0.25 g of uranium in 50 ml of solution. The deposition time decreased approximately fivefold as the current was raised from 2 to 10 amp.

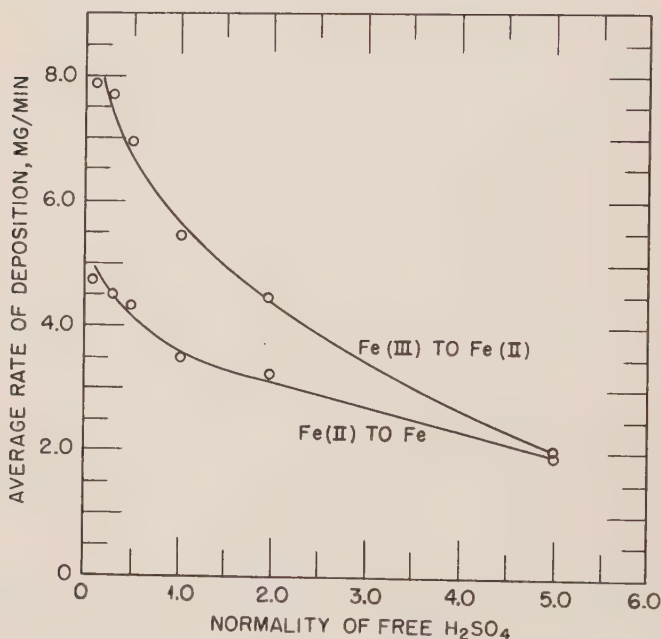


Fig. 23.2—The effect of acidity upon the rate of deposition of iron into the mercury cathode. Electrolyte volume, 150 ml; current, 2 amp; anode, platinum gauze; cathode area, 21 sq cm; stirring, both cathode and electrolyte; Fe, 1 g; U, 0.25 g.

A second set of experiments,^{16,17} performed in a solution more dilute with respect to iron and uranium (1 and 0.25 g per 150 ml, respectively), showed the same phenomenon of increasing deposition rate with increasing current density. Comparable rate increases were noted for chromium and molybdenum when the current density was increased.

It should be mentioned that, although increasing the current density does markedly increase the deposition rate for cations, practical limitations govern the maximum current density applicable to a given

electrolysis. With the samples and apparatus used (see Fig. 23.1), currents of about 10 amp cause a vigorous evolution of hydrogen and oxygen and an excessive heating of the electrode leads. Excessive gas evolution causes the sample to spatter and also constitutes an explosion hazard. Also, many commonly used sources of direct current are not capable of passing a current as high as 10 amp through the type of sample described.

Deposition Rate as Function of Impurity Content of Cathode Mercury. Since it is convenient to reuse the cathodic mercury until the deposition rate begins to be detrimentally affected and since the complexity of the mercury purification process depends upon the purity required, an investigation of the influence of specific amounts of cathode impurity on the deposition rate was made.^{16,17} It was found that when successive iron samples were electrolyzed into the same cathode under identical and approximately optimum conditions of electrolysis, the deposition time became progressively greater until, as the iron level reached 0.5 per cent of the weight of the cathode mercury, the electrolysis times for 2.0-g iron samples and for 0.5-g chromium samples were twice those required for pure mercury cathodes.

Deposition Rate as Function of Type and Speed of Stirring. Smith⁷ and Classen²⁰ have both referred to the importance of rapid stirring in the attainment of fast and complete electrolytic deposition. The influence of the type and speed of stirring on the rate of electrolytic deposition was studied.^{16,17} It was shown that a definite increase in the deposition rate is obtained (1) when the stirring rate is increased, (2) when the stirring is restricted to the mercury (no paddles in the electrolyte layer), and (3) when a platinum spiral anode replaces the platinum gauze.

Deposition Rate as Function of Electrolyte Temperature. High electrolyte temperatures have previously been recommended for increasing the deposition rates and for providing superior deposits.^{7,20} The average deposition rate of 1-g samples of iron also containing 0.25 g of uranium in 150 ml of 1N sulfuric acid was studied at temperatures ranging from 5 to 69.4°C.^{16,17} The average deposition rate increased continuously from 0.0058 g per minute at 5.0°C to 0.0079 g per minute at 40°C; at higher temperatures, however, the deposition rate dropped sharply, reaching only 0.0055 g per minute at 69.4°C. An optimum electrolysis temperature range of 25 to 60°C for a current intensity of 4 amp was indicated by these experiments.

Deposition Rate as Function of Depositatable-cation Concentration. A study has been reported^{16,17} on (1) the electrolysis of a constant

amount of cation from various volumes of electrolyte, (2) the electrolysis of various concentrations of cations from a constant volume of electrolyte, and (3) the deposition behavior as the concentration of depositable cation decreases during electrolysis.

It was shown that, under otherwise optimum and constant conditions of electrolysis from 1N sulfuric acid mediums, the deposition rate of 1 g of iron (in the presence of 0.25 g of uranium per 150 ml) increases steadily with decreasing volume until a volume of 50 ml is reached. Further decrease in volume has little effect.*

When increasing amounts of iron and chromium were electrolyzed in a constant volume, an increase in current efficiency was also noted. Under the conditions used (optimum, except that the current was only 3 to 4 amp) the deposition rates increased with increasing cation concentration until the concentration reached 20 g per liter for iron and 10 g per liter for chromium. In the former instance the average rate of deposition more than quadrupled as the iron concentration of the samples was increased from 2 to 20 g per liter. The chromium deposition rate more than doubled when its concentration was raised from 2 to 10 g per liter. For both elements, further increases in the concentration caused no appreciable improvement in the deposition rate.

The deposition status at different times during an electrolysis of iron performed under optimum conditions is shown in Fig. 23.3.^{16,17} The curves for chromium and molybdenum are similar but do not rise so steeply.

Deposition Rate as Function of Uranyl Ion. Furman, Haight, and McDuffie²¹ have reported that the electrolytic deposition of iron is greatly retarded and the deposition of chromium and molybdenum is almost prevented by the presence of 10 g of uranium in the electrolyte. Similar findings as to iron and chromium have been made.^{16,17} The interference of lesser quantities of uranium on the electrolysis of iron and chromium was also studied. An approximate doubling in deposition time for 1-g iron samples was noted when the uranium concentration was increased from 0.24 to 1.9 g per 50 ml. When 0.5-g chromium samples were similarly electrolyzed, the addition of 0.25 g of uranium increased the deposition time by about 30 per cent, while the addition of 1.5 g of uranium added 170 per cent to the time required in the absence of uranium. Except for the uranium content, electrolysis conditions for these experiments were optimum. The increase in deposition time due to uranium is undoubtedly caused,

*Smith has reported the quantitative deposition of 0.2 g of iron in a 5-ml volume in as little as 7 min from samples containing no uranium.

in part, by the time required to reduce uranium(VI) to uranium(IV), but Furman, Haight, and McDuffie have suggested²¹ that uranium acts as an oxidation-reduction buffer in mercury-cathode electrolyses. At equilibrium the cathode approximates the potential of the uranium (III)/(IV) couple when the uranium content is high. The resultant potential is apparently not high enough to deposit chromium or molybdenum.

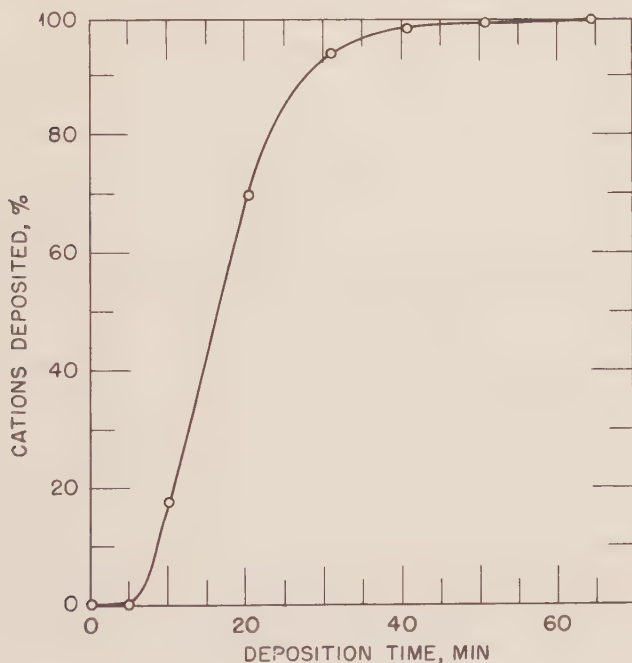


Fig. 23.3—Deposition of iron into the mercury cathode as a function of time. Electrolyte volume, 50 ml; acidity, 1.0N; current, 5.0 amp; anode, flat platinum spiral; cathode area, 21 sq cm; stirring, cathode only; Fe, 0.962 g; U, 0.25 g.

Deposition Rate as Function of Phosphate Ion. Although phosphate does not appear to increase the electrolytic deposition time for iron,^{16,17} its presence in the electrolyte in high concentrations is undesirable, because the uranium(IV) phosphate is precipitated from weak sulfuric acid solutions.

(b) Electrolysis from Perchloric Acid Mediums. Some workers¹⁶ compared perchloric acid with sulfuric acid as an electrolyte for the mercury-cathode electrolysis. Under identical electrolysis conditions

(optimum for sulfuric acid), samples containing 1 g of iron and 0.25 g of uranium were electrolyzed in 1N perchloric acid and in 1N sulfuric acid.

The deposition time for iron in perchloric acid medium was about 10 per cent longer than the time required in sulfuric acid solution. Similar experiments with the same acid concentration and uranium content were performed with samples containing 0.25 g of copper, 0.25 g of nickel, 0.10 g of chromium, or 0.10 g of zinc. In all instances the deposition time was increased only slightly when 1N perchloric acid was used as the electrolyte.

1.2 Use of Mercury Cathode in Determination of Impurities in Uranium Compounds. Although Lundell and Hoffman²² state that "so many elements are deposited that the method finds very restricted application in determinations of the elements," Furman and his co-workers^{21,23-26} developed a procedure for the determination of trace impurities in uranium and its compounds. This method involves electrolysis into the mercury cathode, followed by the subsequent recovery of the impurities from the mercury and their polarographic determination.

The procedure evolved by these investigators^{23,24} calls for the electrolysis of a concentrated uranyl sulfate solution containing only the amount of free sulfuric acid required for the reduction of the hexavalent uranium to the quadrivalent state (see Eqs. 5 and 5a). Excess acid is undesirable, for it inhibits the reduction of quadrivalent uranium to the trivalent form (see Eqs. 6 and 6a), this reduction, according to Bricker and Furman,²⁴ being essential for the complete deposition of elements such as iron. The effect of anodic oxygen on the reduction of uranium to the trivalent state is minimized by the use of a straight platinum-wire anode (not larger than 15 gauge) immersed no more than 1 cm into the electrolyte.

Electrolyses are carried out on samples containing 7 to 10 g of uranium in a volume of about 125 ml, with an applied potential of 10 volts and a current of about 0.8 amp. The electrolysis is continued for 1 or 2 hr after the electrolyte turns red in color, thus indicating the reduction of a significant amount of quadrivalent uranium to the trivalent form.

After electrolysis the mercury is withdrawn from the cell and transferred to a small silica boat, which is then placed in a horizontal tube furnace. The mercury is distilled in a stream of nitrogen, and the residue of impurities in the boat is dissolved and analyzed polarographically.

In order to determine the recovery of known amounts of impurities from uranium solutions by this method, Furman et al.²¹ electrolyzed

samples containing 10 g of uranium as the sulfate and 0.02 to 2.0 mg of each known impurity, both individually and in combination. The distillation residues from these samples were analyzed polarographically or colorimetrically in order to determine the degree of separation of the electrolyzed impurities. As a result of their work the investigators concluded that cadmium, cobalt, copper, iron, nickel, lead, and zinc are quantitatively deposited into the mercury cathode from solutions containing large amounts of uranium, whereas chromium, manganese, and molybdenum are not deposited appreciably, if at all, under the conditions of these electrolyses. In addition, it was stated that bismuth, indium, and thallium are probably deposited quantitatively into the mercury cathode, although iridium and ruthenium are perhaps not deposited. Inconclusive results were obtained for gallium, gold, palladium, rhenium, selenium, and tellurium. Bricker and Furman²⁴ also used the nitric acid electrolysis of bismuth⁷ as an analytical separation.

1.3 Techniques and Equipment for Minimizing Anodic Oxidation.

(a) Partial Immersion of Platinum-gauze Anode. An investigation of the optimum degree of immersion of a platinum-gauze electrode was made.¹⁶ It was found that the average rate of reduction from iron(III) to iron(II) increased from 0.0055 g per minute for the fully immersed anode to 0.026 g per minute in a test in which only the edge of the gauze contacted the electrolyte. The deposition rate for the reduction from iron(III) to iron(0) increased from 0.0036 g per minute at full immersion to 0.0045 g per minute at slight immersion.

(b) Platinum Spiral Anode and Platinized Platinum Anodes. The so-called "flat platinum spiral anode,"²⁰ fabricated from coiled 16-gauge platinum wire, was found to have a slight superiority over the small-immersion gauze anode. The spiral type of anode is better also from the standpoint of cost, simplicity of fabrication, and ease of cleaning.

Inasmuch as the use of platinum-black electrodes is said to minimize the formation of $\text{H}_2\text{S}_2\text{O}_8$ in sulfuric acid electrolyses,¹⁹ the possibility that the use of platinized platinum would minimize anodic oxidation was tested. A series of 12 electrolyses¹⁶ with platinized and nonplatinized anodes indicated some superiority for the platinized anodes, particularly the platinized spirals. It was decided, however, that the saving in time effected by using platinized electrodes would not justify the time, expense, and care involved in their preparation and handling.

(c) Separate Anode Compartment. A modified mercury-cathode cell, with a separate anode compartment as shown in Fig. 23.4, has been employed by Gantz, Barnhart, De Vries, and Mellon²⁸ for the purification and reduction of uranium solutions.

It should be mentioned that a very rapid reduction of uranium is obtained with the anode-compartment cell because no anodic oxygen is stirred into the electrolyte and the transfer of persulfuric acid to the cathode area is probably very small. However, the utility of this

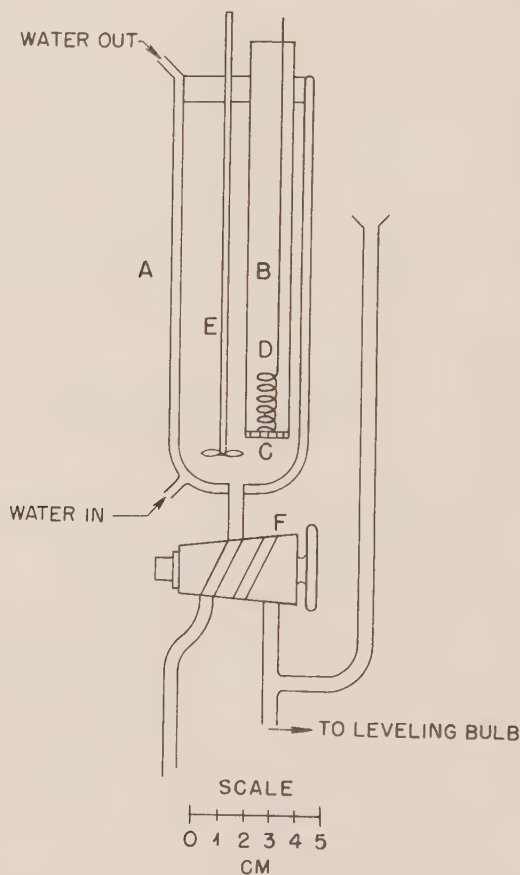


Fig. 23.4—Mercury-cathode electrolysis cell with anode compartment. A, electrolysis cell; B, anode compartment; C, sintered-glass disk of medium porosity; D, spiral of 18-gauge platinum wire; E, stirrer; F, 2-mm two-way stopcock.

electrolytic cell is limited by two factors: (1) the relatively high resistance of the sintered disk limits the current that can be passed through the cell with the usual power sources, and (2) when a head of sulfuric acid is maintained in the anode compartment, a slow flow of acid into the sample increases its volume and thereby decreases the rate of deposition of impurities.

2. ELECTROLYTIC DEPOSITION OF URANIUM ON SOLID METAL CATHODES

The platinum cathode has been employed extensively in the electrodeposition of many metals.^{7,20} The metal is generally deposited in the elemental form. In the case of uranium, however, a hydrated oxide of variable composition or a fluoride is deposited on the cathode. Although this deposit is not satisfactory for the accurate electrogravimetric determination of uranium, it is of use in the preparation of thin films of uranium for the determination of isotopic ratios by measuring the rate of emission of alpha particles and fission products, the latter under the influence of slow-neutron bombardment of standard intensity.

2.1 Deposition of Uranium on Platinum. The rates of alpha-particle emission per unit weight of the various uranium isotopes vary widely. The possibility that this fact might be used as a basis for a method of isotopic analysis of uranium was recognized at an early date.^{29,30} The method involves the counting, under definite conditions, of the numbers of alpha particles emitted per unit time for known amounts of uranium. One of the most important factors in attaining a high degree of accuracy in this method is the preparation of the sample in a thin, uniform film on a metallic base such as a platinum disk.

Three criteria have been suggested by Hull³¹ as aids in judging when a satisfactory film for alpha counting has been prepared. First, the surface of the film should appear smooth and shiny. A smooth and continuous film is indicated, especially in films containing less than 0.2 mg of uranium oxide per square centimeter, by bright interference colors. Such films are usually extremely adherent to their base; they cannot be rubbed off with soft paper, while a dull film can usually be at least partially removed by such treatment. Second, the film must appear smooth and continuous at a magnification of 100 diameters. This magnification makes visible a particle of dimensions equal to the range of the alpha particle, and irregularities in the surface should be of a smaller magnitude than this. Third, the thickness must not vary excessively from one part of the disk to another if an accuracy of ± 0.1 per cent is to be obtained in the determination. A uniform appearance throughout the film indicates a uniformity well within the requirements for thin films. An "exploring disk" is used to check the uniformity of thicker films (0.2 to 0.7 mg/sq cm). This disk has six holes of equal diameter arranged symmetrically about a center hole in a hexagonal pattern, with a small flanged cover for each hole. The disk is mounted on top of the film, one of the six lids is removed,

and the escaping alpha particles are counted. Variations between the counts for the different sections of the disk are taken as a measure of the variations in the thickness of the film.

Hull³¹ has determined that the maximum allowable variation in thickness (expressed as standard deviations) to yield an accuracy of ± 0.1 per cent ranges from 51 per cent for films of 1 mg/sq cm down to 11 per cent for films of 20 mg/sq cm.

As early as 1879 the electrolytic deposition of uranium as a film on platinum was investigated by Smith,³² and since that time several papers have been published on the subject. The electrolysis of an aqueous solution of uranyl salt deposits uranium on the cathode as a hydrous oxide. Differences of opinion have existed, however, as to the chemical composition and physical properties of the plated material.

Heal³³ states that the properties of the deposit vary according to the conditions. If the solution is nearly neutral (with a pH of about 6), a fluffy yellow oxide having the composition of a hydrated UO_3 forms rapidly at the cathode, but most of it fails to adhere and falls to the bottom of the vessel. If the solution is somewhat more acid, with a pH near 3, the deposits may be green or black. These deposits will contain more or less of the lower oxides, approximating the compositions U_3O_8 and UO_2 .

Pierle,³⁴ in his extensive investigation of the electrochemistry of uranium, repeated Smith's work, in which the uranyl acetate, nitrate, or sulfate was electrolyzed onto a platinum-disk cathode, and found that the uranium deposit, when ignited at 700°C , contained more oxygen than is expressed in the formula U_3O_8 . He concluded that uranium is deposited as a poorly adherent oxide of variable composition. His data also indicated that appreciable quantities of sodium and potassium, if present in the electrolytic medium, are codeposited with the uranium. Coomans³⁵ corroborated Pierle's data, finding variations of several per cent in the composition of the plated uranium oxide.

None of these deposits would have been suitable for alpha counting, however, even if they had been deposited on a plane surface, for they were thick, coarse, and uneven. The first satisfactory films appear to have been prepared by Francis and Tcheng-da-Tchang,³⁶ who used electrolytic mediums containing ammonium acetate and alcohol-water mixtures. These deposits were in the form of a thin, uniform film that showed interference effects and had considerable metallic luster. The films were adherent when less than 0.2 mg of U_3O_8 was deposited per square centimeter of platinum disk; heavier deposits peeled. These investigators deposited only a fraction of the uranium present in the cell solution and assumed that ignition at 700°C converted all the uranium to U_3O_8 .

Cohen and Hull³⁷ made a study of the conditions necessary for obtaining a smooth, uniform film of uranium oxide by electroplating on platinum. At first these investigators ignited the uranium films and based their isotopic analysis upon the weight of U_3O_8 thus obtained. It was found that this method did not yield the desired accuracy of 0.1 per cent. The assumption of constant composition of the U_3O_8 was avoided, and the time-consuming weighing operation was eliminated, by quantitatively plating out a known amount of uranium.

In order to discuss the deposition of uranium in more detail it is desirable to consider the type of electrolytic mediums employed. These mediums include sodium or ammonium acetate with acetic acid buffer, ammonium oxalate, and sodium fluoride solutions.

(a) Deposition of Uranium from Ammonium Acetate-Acetic Acid Mediums. The first uranium oxide films prepared by Cohen and Hull³⁷ were made in a simple electrolytic cell that consisted of a 150-ml beaker containing a buffer solution of sodium or ammonium acetate and acetic acid. The use of sodium acetate was shown to give low-count results owing to contamination of the deposit with nonvolatile sodium oxide.

Their method produced films that possessed the properties of being highly uniform, shiny in appearance, extremely adherent, and absolutely smooth at a magnification of 100 diameters. These films also had uniform interference colors and gave the same alpha count over all portions of their surface. However, the quantity of uranium that could be deposited in this apparently excellent condition was limited to less than 4 mg. If heavier films were prepared, microscopic striations appeared and developed into cracks, along which the films began to peel.

In spite of the great care exercised a considerable proportion of the films differed widely (up to 1 per cent) from the average. A number of variables were studied in an effort to locate the cause of the difficulty. It was found that blank disks, prepared by the electrolysis of solutions containing no uranium, gave both positive and negative weight changes. It was therefore necessary to obtain the weight of uranium per disk by reweighing the disk after the film had been counted and dissolved. Even with these and other refinements, however, it was found that the reproducibility of the weighed films was still only about 0.25 per cent. The failure to obtain more accurate results with improved technique indicated that the films varied in composition, so that a direct weighing was an inexact method of determining their uranium content. At this point, where otherwise it would have been necessary to discard electroplating as an accurate method, Cohen and Hull³⁷ studied the quantitative plating of a known

weight of uranium in a uniform adherent film from an ammonium oxalate medium.

(b) Deposition of Uranium from Ammonium Oxalate Medium. For the development of a quantitative electroplating method from an ammonium oxalate medium, Cohen and Hull³⁷ employed an electrolytic cell (see Fig. 23.5) similar to the one used by Francis and Tcheng-da-Tchang.³⁶ This cell was used in a study of the effect of various factors.

(1) Effect of Various Factors on Rate of Plating. Ordinary variations in electrolytic conditions will affect the rate and completeness of plating as well as the composition of the deposit. The effects of various factors upon the rate of plating in the ammonium oxalate method were studied.³⁷ The percentage of uranium deposited was determined, under the chosen conditions of electrolysis, by counting the alpha particles from the film and comparing the weight of uranium calculated therefrom with the weight of uranium in the original sample. When the deposition of uranium approached 100 per cent, the alternative procedure of determining the uranium remaining in the cell solution was used. The results of this investigation are shown in Table 23.1.

The percentage of the uranium deposited as a function of time is shown by the data of series 1 in the table. A logarithmic graph of these data indicates that the electrolysis tends to follow a first-order rate law.

Series 2 in the table shows the effect of current density upon the percentage of the uranium deposited. It will be observed that an increase in current density causes an increase in the rate of plating.

The effect of temperature on the rate of plating is shown in series 3 in the table. The recorded temperatures were those of the water bath with which the plating cell was surrounded. The temperature of the electrolyte was somewhat below these values during the initial stages of the electrolysis, but soon thereafter it rose to about 10°C above the temperature of the bath.

The rate of stirring has some effect upon the rate of plating, as indicated by the data of series 4 in the table. An increase in the rate of stirring, up to the limit set by the centrifugal effect on the solution, causes an increase in the rate of plating. The use of higher rates of stirring results in a nonuniform radial distribution of the film. This effect can be counteracted to some extent by increasing the concentration of the ammonium oxalate, but at the expense of a serious reduction in the rate of plating. A compromise at about 500 rpm results in a film that is thin at the center but reproducible to a high degree with only moderate control of the rate of stirring.

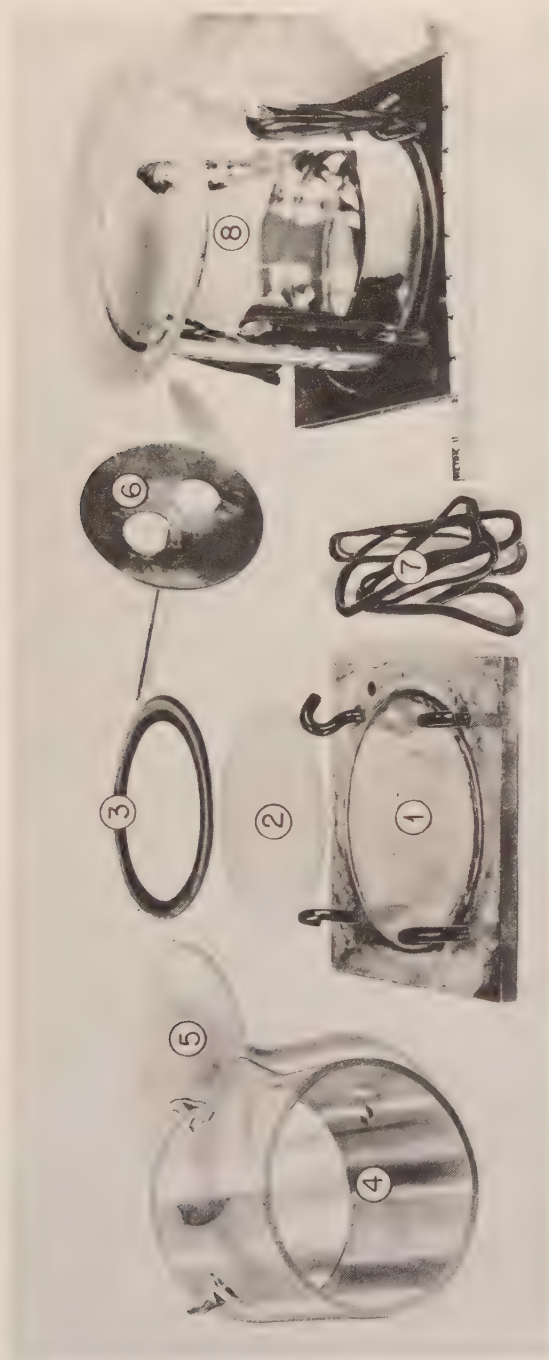


Fig. 23.5—Electrolysis cell for the deposition of uranium. 1, stainless-steel holder; 2, platinum disk; 3, Vinylite or bleached rubber gasket; 4, glass cylinder; 5, split watch glass; 6, platinum anode; 7, strong rubber bands; 8, assembled cell.

The effect of varying amounts of ammonium oxalate in the electrolyte upon the rate of plating is shown in series 5 in the table. It will be noted that an increase in concentration causes a decrease in the rate of plating. The films made with the larger quantities of ammonium oxalate, however, showed more desirable properties, such as

Table 23.1—Effects of Various Factors upon the Rate of Plating

Series No.	Sample of U salt	Ammonium oxalate, millimoles	Anode stirring, rpm	Temperature, °C	Current, amp	Time, min	Uranium deposited, %
1	6 mg of sulfate	2.0	500	80	3.0	3.0	56
						5.0	82
						7.0	93
						10.0	98.4
						15.0	99.9
2	6 mg of sulfate	2.0	530	80	0.50	5.0	18.0
					1.00		42.0
					2.25		69.2
					3.00		81.5
					4.00		88.2
3	6 mg of sulfate	2.0	530	25	3.0	10.0	17.2
				40			45.8
				50			58.4
				60			88.0
				70			96.6
				80			98.4
				95			99.3
4	4 mg of nitrate	1.0	250	60	3.0	10.0	60.3
			480				71.5
			970				86.7
5	6 mg of sulfate	1.0	500	80	3.0	5.0	81
		2.0					82
		3.0					67
		4.0					63
Standard method	6 mg of nitrate	2.0	500	80	3.0	50	99.98

uniformity, metallic luster, and adherence. The films prepared from electrolytes containing 2 millimoles of ammonium oxalate were sufficiently satisfactory to allow their use for precision counting.

The effect of the composition of the electrolyte upon the rate of plating is rather small. The rate of plating decreases by about 10 per cent for each solute as the ammonium salt is changed from the acetate to the oxalate and the carbonate. Of these three salts, the oxalate gives by far the best type of electrodeposit. This deposit is adherent

and possesses considerable hardness. The deposits obtained from electrolytes containing ammonium nitrate or sulfate are uneven, brown, and powdery and are not very adherent. These films do not show the usual interference colors of films prepared from electrolytes containing the organic anions previously mentioned. It is interesting to note, however, that a satisfactory film may be obtained by the electrolysis of a uranyl nitrate or sulfate salt in the presence of ammonium acetate, provided that the molar ratio of the anion to the acetate is not much greater than 1 to 100. If ammonium oxalate is used, considerably higher concentrations of nitrate or sulfate (about 1 to 1) may be present in the electrolyte.

The rate of plating, as well as the maximum thickness of the plate that can be deposited on a platinum disk, depends upon the conditions of the surface of the disk. The rate of plating, as well as the upper limit of U_3O_8 per square centimeter of surface, increases in this order: etched, cold-rolled, and polished platinum. The greatest difference lies between the etched platinum and the other two types. The rate of plating is also affected by the kind of metal disk used as the cathode. A decrease in the plating rate of about 10 per cent seems to occur for each of the following metals in the order given: silver, platinum, copper, and tin, when these metals are used in the form of bright foils.

(2) Effect of Various Factors upon Composition of Electrodeposit.

A modification of the electrolytic cell employed by Cohen and Hull has been reported by Cameron and Morris.³⁸ It is illustrated in Fig. 23.6. This plating cell employs a cylinder of polystyrene plastic instead of the more fragile glass cylinders used by earlier investigators. A stainless-steel base is threaded to screw onto the bottom of the plastic cylinder. This simplicity of design allows the cell to be easily assembled and disassembled without the use of the usual rubber bands or bolts. The plastic cylinder is 4 in. high, with an outside diameter of 2½ in. and an inside diameter of 2¼ in. The plastic is said to whiten somewhat with continued use at 80°C, but it shows no signs of retention of uranium.

Procedure.³⁷ The individual parts of the cell, as well as the assembled cell (Fig. 23.5), are cleaned (the latter being done immediately before plating) by rinsing momentarily with chromic acid. Two millimoles of 0.4M ammonium oxalate are pipetted into the cleaned cell, followed by a known weight of uranium in the form of a uranyl salt in aqueous solution.

The solution of the uranyl salt may contain any anion that does not attack platinum during the electrolytic process (nitrate, acetate, sulfate, and fluoride have all been used successfully), but it should not contain large amounts of free acid. Acid in molar concentrations

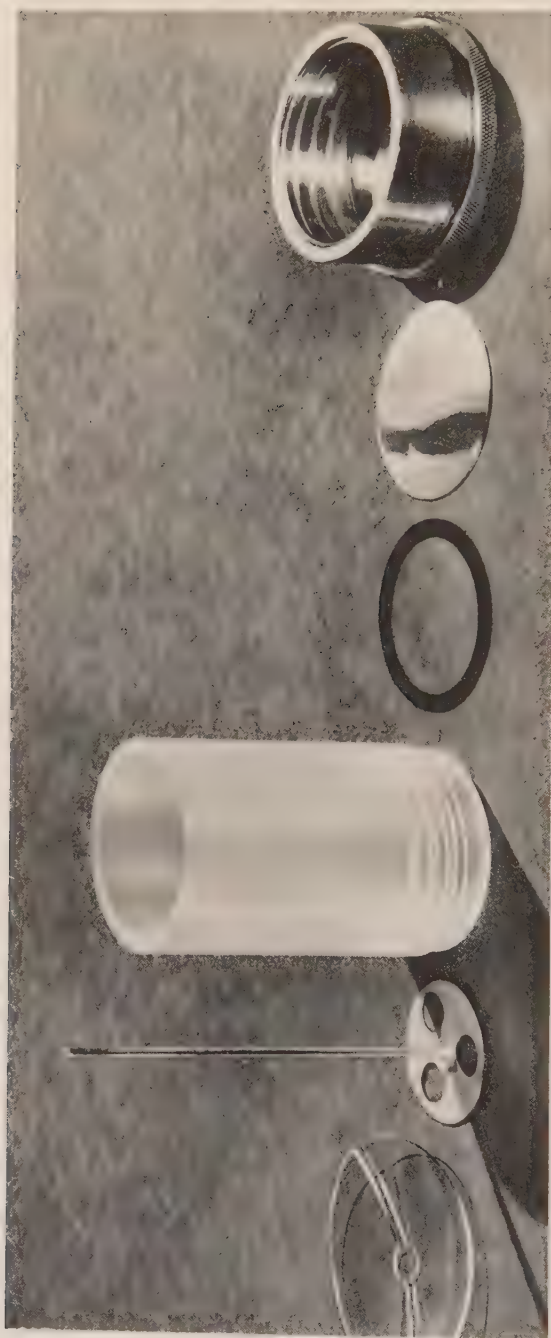


Fig. 23.6 —Cell for the deposition of uranium, employing a polystyrene plastic cylinder and a stainless-steel base cap.

equivalent to the uranyl salt present may be tolerated, but not in much higher concentrations. Whenever appreciable amounts of acid are left behind in the method of preparing the uranyl salt, enough ammonium hydroxide is added with the ammonium oxalate to neutralize the free acid. For best results it is recommended that as little free acid as possible be present in the original uranyl solution.

The total volume of the plating solution is adjusted to approximately 30 ml, and the cell is placed in a water bath at about 80°C. The platinum anode is dipped a few millimeters below the surface of the plating bath, the cell is covered with split watch glasses, and the anode is rotated at about 500 rpm. A current of 3 amp is used for a cell with a cross-sectional area of 23 sq cm, the voltage drop at the beginning of the electrolysis being 8 to 10 volts.

The electrolysis is carried out for 20 to 50 min; about halfway through this period the watch glass and the sides of the cell are washed down with a few milliliters of water. At the end of the electrolysis the contents of the cell are poured immediately into a beaker and are later tested for uranium. Sometimes 60 ml of methyl alcohol is added to the plating bath before the current is broken. The alcohol acts as a rinse and also helps to leave the cell dry when it is drained. The cell is taken apart, and the platinum disk is ignited for 5 min at 700°C, after which it is ready for counting.

The quantitative plating method described above has the following advantages over methods previously used: (1) the accuracy is better than 0.1 per cent, as compared with 0.3 per cent for weighed electroplated films; (2) the tedious task of weighing individual plates precisely, both with and without films, is eliminated; (3) the amount of sample needed for an analysis is greatly reduced, and the total sample may be recovered from the platinum disk; and (4) the demand on the operator's time is greatly reduced, since only an occasional inspection, rather than constant attention, is required during the plating.

(c) Deposition of Uranium from Sodium Fluoride Medium. Kahn³⁹ and Lilly^{40,41} deposited uranium from an electrolytic medium containing sodium fluoride, employing an electrolytic cell (see Fig. 23.7) similar to that used by Cohen and Hull.³⁷ The main differences in construction were the use of a flat spiral of platinum wire instead of a platinum disk as a stirrer-anode and the use of bolts to hold the cell together. A platinum "frying pan" was placed beneath the platinum cathode for electrical contact. The original method consisted of the reduction of uranium to the quadrivalent state in a sodium fluoride medium and the subsequent plating of the uranium on the cathode as UF_4 . The deposit was ignited to U_3O_8 , and the specific activity determination was based upon the weight of this deposit.

The deposition of about 0.5 mg of uranium was obtained from an electrolyte 10 to 15 ml in volume and 0.05N to 0.10N in sodium fluoride, using platinum-disk cathodes $1\frac{1}{2}$ in. in diameter. The sodium fluoride was usually added as 2 ml of a 1 per cent solution at the beginning of an electrolysis, followed by an additional milliliter after

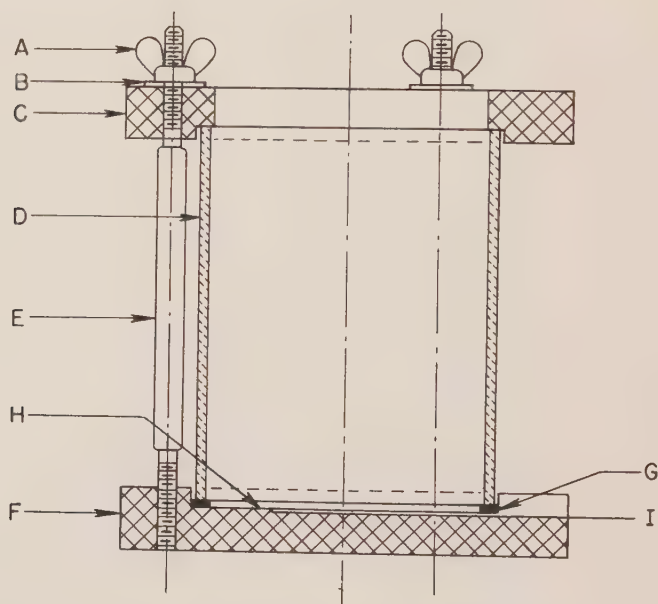


Fig. 23.7—Electrolytic cell used for the deposition of uranium from a sodium fluoride medium. A, brass wing nut; B, brass washer; C, Lucite top collar; D, 3-in. pyrex tube; E, brass stud; F, Lucite bottom collar and plate; G, neoprene gasket; H, platinum disk; I, platinum conductor.

1 hr. The electrolysis was carried out at room temperature with a current of 50 ma. The coiled platinum-wire stirrer was found to be the most satisfactory means of stirring despite the pattern of concentric rings that it produced on the cathode. The stirrer was rotated at a moderate rate of speed 0.25 in. above the platinum-disk cathode.

Lilly⁴¹ also eliminated the time-consuming weighing of individual disks by his development of a more accurate procedure based on the quantitative deposition of a known amount of uranium contained in a known volume. A procedure was devised which involved the accurate measurement of an aliquot of a uranium solution and the quantitative deposition of the uranium contained therein.

The first condition was met by dissolving the sample (20 to 200 mg of pure U_3O_8) in a minimum amount of HNO_3 , diluting to volume in a volumetric flask, and removing an aliquot with a pipet. By choosing the correct combination of flask and pipet it proved possible to obtain films of approximately 0.5 mg regardless of the weight of the original sample. By this procedure the amount of uranium on the disk could be calculated solely on the basis of the weight of the original sample of U_3O_8 and the fraction of the whole amount taken for electrodeposition.

Obviously, the accurate measurement of the aliquot is useless unless the uranium is deposited quantitatively on the platinum disk. This assurance was obtained by carrying out the deposition as usual and then running a fluorescent-bead test on the cell solution before discontinuing the electrolysis. In a solution containing approximately 0.5 mg of uranium in a volume of 15 ml, a bead test showing 0.25 γ of uranium per milliliter would indicate sufficiently complete deposition for the desired accuracy. The electrolysis may then be discontinued, and the platinum disk ignited and counted.

(d) Deposition of Uranium on Copper. A copper cathode and a rotating platinum anode have been employed by Cook⁴² for the electrodeposition of uranium from ammonium acetate-acetic acid buffer solutions. This investigator determined the effect of temperature on the deposition of uranium from electrolytes of 100 ml volume, 0.5M in ammonium acetate and 0.01M in uranyl nitrate. A current of 0.15 amp per square decimeter was used, and the electrolysis was carried out for 50 min. The amount of uranium deposited was calculated from the difference in the alpha activity of equivalent samples of the original and the electrolyzed solutions. Cook found that increasing the temperature from 38–47°C to 86–90°C produced progressively increased deposition varying from 35 per cent at the low range to 99 per cent at the high.

Cook also studied the effect of acidity on the deposition of uranium. He employed solutions of 100 ml volume and 0.01M in uranyl nitrate at various hydrogen-ion concentrations. The solutions were electrolyzed for 50 min at a current of 0.15 amp per square decimeter. The temperature was controlled at 79 to 87°C. It was observed that the uranium deposit adhered more firmly to the cathode as the acidity was increased below a pH of 5. At this pH, however, the deposit flaked off readily during the electrolysis.

(e) Deposition of Uranium on Nickel. Jenny,⁴³ in an adaptation of the work of Cohen and Hull,³⁷ employed a nickel cathode and a rotating platinum-disk anode for the electrodeposition of uranium from an ammonium oxalate medium. The purpose of Jenny's work was to speed up the routine operations of the counting method of isotopic

analysis by making larger and thicker films of uranium oxide. He plated a 44.5-sq cm film on a disk of 0.005-in. cold-rolled nickel $3\frac{5}{16}$ in. in diameter. The plating apparatus was similar to the one used by Cohen and Hull, except that it was larger in order to accommodate the larger cathode. The cell stack was made of standard 80-mm glass tubing and was $2\frac{1}{2}$ in. high. The platinum stirrer-anode was a disk, 70 mm in diameter and 0.020 in. thick, attached to a platinum rod. The cell base plate was constructed of brass in order to permit good conductance of heat both in and out of the plating cell. The assembled cell was heated by means of a water bath.

Procedure.⁴³ The nickel disks are cleaned with acetone and then allowed to remain in an ethylene trichloride Soxhlet for at least 1 hr. The cell is thoroughly rinsed, and 8 millimoles of ammonium oxalate is added. Two to forty milligrams of uranium is added, the volume is adjusted to 75 ml, and the electrolysis is carried out for 50 min at a temperature of 80°C. A current of 6 amp is used, with a stirring rate of 500 rpm. After 25 min of electrolysis the anode and cell walls are washed down with 10 ml of water. When the deposition of uranium is complete, the disk and film are removed and ignited at 425°C for 5 min. The disk is then ready for alpha counting.

Uranium films prepared in this way are said to be adherent and to appear as uniform as films prepared on the 23-sq cm cathodes. It was found that the deposition of uranium was 99.99 per cent complete under the conditions outlined above. Jenny also found that the deposition of 10-mg aliquots of U_3O_8 was more than 99 per cent complete after 15 min of electrolysis.

A modification of the Jenny procedure has been employed by Bird-sall and Klacsmann⁴⁴ for the analysis of uranium hexafluoride. The hexafluoride is condensed in a cold platinum trap, where it is then hydrolyzed. The uranyl fluoride solution formed is evaporated to dryness and ignited to U_3O_8 . The sample of U_3O_8 (50 to 500 mg) is dissolved in nitric acid, and an aliquot containing 2 to 10 mg of U_3O_8 is taken for plating. The uranium is plated on a 60-sq cm nickel disk from ammonium oxalate mediums.

(f) Electrodeposition of Thorium on Solid Metal Cathode. Films of ThO_2 have also been prepared by deposition on a platinum cathode.⁴⁵ A solution containing $Th(NO_3)_4$ and a relatively small amount of $K_4Fe(CN)_6$ is electrolyzed. The deposited film on the cathode, which is assumed to be $ThFe(CN)_6$, is ignited to a mixture of iron and thorium oxides. The iron oxide is leached out of the composite film, a thin film of ThO_2 being left on the platinum disk.

Procedure.⁴⁵ The apparatus used was the same that Kahn³⁹ used for making films of uranium. Four milliliters of $K_4Fe(CN)_6$ solution

[0.1 g of $\text{K}_4\text{Fe}(\text{CN})_6$ in 200 ml of water] and 16 ml of $\text{Th}(\text{NO}_3)_4$ solution [5 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in 100 ml of water] are added to the electrolytic cell, and the solution is electrolyzed at 3.5 volts and 50 ma for about 30 min with constant stirring. The platinum plate is removed and, after being washed well with water, is ignited over a bunsen flame. The plate is then placed in a dish of 12N HCl and heated over a steam bath for 30 min to remove the iron oxide. This process should be repeated with fresh 12N HCl and a heating time of 15 min. Almost all the iron should be dissolved off the plate following this treatment. Some ThO_2 will be removed by the leaching process. If a thicker film is desired, the plate is remounted in the cell and the entire procedure repeated. This repetition is necessary in order to build up a thick plate. By varying the electrolysis time from 0 to 30 min a very thin film can be obtained.

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Chapter 24

PHOTOMETRIC METHODS

By M. Fred and C. J. Rodden

1. INTRODUCTION

Spectrophotometric and colorimetric methods of analyses have been used for the determination of elements in solution in the form of dissolved, highly colored compounds or complexes. Infrared spectrophotometry has been used for the analysis of hydrocarbons and fluorocarbons and for measuring the concentration of fluorocarbon in air. Spectrophotometric methods using the visible and ultraviolet region of the spectrum have been employed in various applications such as the determination of oxidation states or the analysis of organic materials.

Fluorescence methods with accompanying photoelectric measuring instruments have been investigated and applied to the determination of traces of uranium and fluoride.

2. LAWS OF ABSORPTION

The monograph "Colorimetry for Chemists," by M. G. Mellon, reviews the theory of and the instruments in general use in colorimetry.¹ In photometric methods the amount of colored material present is determined by measuring the fraction of light absorbed in passing through a known depth of solution. The fraction transmitted is given by the Lambert-Beer law

$$\frac{I}{I_0} = 10^{-kcb} = 10^{-D} \quad (1)$$

where I_0 is the intensity of the light beam transmitted by the solvent or blank, I is the intensity of the light beam transmitted by the solution, k is a constant (specific extinction) for which the value for spec-

ified units depends upon the solvent and the temperature as well as upon the wavelength of the light, c is the concentration of the colored substance, and b is the length of the absorbing path in the solution. The product kcb , which is equal to D , is called the "optical density" (sometimes "extinction"); it is a linear function of concentration, whereas transmittancy, I/I_0 , is a logarithmic function of the concentration. If the concentration is expressed in moles per liter and the depth is expressed in centimeters, k becomes the molar or the molecular extinction coefficient, usually designated ϵ . If the concentration is expressed in other units, such as micrograms per milliliter, the numerical value of the extinction coefficient, denoted in general by K , must be altered by the appropriate conversion factor to yield the same numerical product for the density. It is therefore apparent that all units must be clearly designated. Some light loss occurs in the absorption cell used to hold the solution, and in practice this loss is corrected by balancing against an identical cell containing the pure solvent, or better, by balancing against a solution containing all substances except the colored substance that is formed by the element in question. The measured quantity I/I_0 therefore refers to the solution itself and is called specifically the "transmittancy," whereas the term "transmittance" includes cell losses, reflection losses in case the sample is a glass filter, etc. In this volume "transmittancy" has been used to a greater extent than "optical density."

The value of the extinction coefficient may vary with wavelength, indicating absorption bands that may be wide, covering several hundred millimicrons, or narrow and perhaps with considerable structure. The wavelength interval, necessarily finite, over which the transmittancy is measured must be small compared with the width of the absorption peak, where the density is reasonably constant; otherwise a fraction of the absorption wings will be included, and the average density so measured will be less than the true density at the peak. This will have the effect of reducing the sensitivity. It may also cause an apparent failure of Beer's law since the shape of the band, which is measured in terms of transmittancy, is distorted as the concentration is changed, and therefore the fraction of the wings included in the measured wavelength interval is changed. For wide bands this restriction on the measurement interval is not at all severe and can often be satisfied by the use of filters or even by the color discrimination of the eye. For very narrow bands, e.g., those found with the rare earths, it may be impossible with a given spectrophotometer to include only the wavelength interval near the peak, and spectrographic methods may be necessary. Fortunately, the effective slit

width of a good modern spectrophotometer can be made sufficiently narrow in most wavelength regions for practically all analytical applications.

Another common cause of apparent failure of Beer's law is lack of proportionality between the total amount of a given element present in solution and the amount present in the form giving rise to the light absorption, owing to dissociation, association, solvation, etc. An empirical calibration covering the range of concentrations to be measured is usually necessary.

For analytical purposes an important consideration is the interference of other elements with the one being determined. The effect may be purely optical in that additional light absorption is contributed, or the interference may be essentially chemical in nature. Examples of the latter are the presence of other ions that form precipitates under the conditions at which the color reaction is produced, thereby introducing the possibility of loss of the element to be determined, and the presence of other ions that complex the element so that no colored product is formed. It may be possible to remove chemical interferences by alteration of the conditions of the procedure, such as change of pH, if such latitude is permissible, or by adding complexing agents that selectively complex the interfering ions. If alteration is not effective and no other method of determination is available, a chemical separation of the interfering ions is necessary.

The optical interference resulting from light absorption by other ions can sometimes be eliminated by a suitable choice of reagent used to produce the colored product. Unfortunately, however, specific reagents are rather rare. In most cases reagents are merely selective since similar products are usually formed with ions of similar size and charge. In such cases it often happens that the absorption spectra of similar ions with the same reagent are sufficiently different to permit the determination of the concentration of each by the ordinary method for the spectrophotometric analysis of multicomponent mixtures, and it is therefore unnecessary to effect a chemical separation. This procedure^{2,3} is based on the fact that the densities of the individual components are additive; therefore at any one wavelength the following relation is true:

$$D(\lambda_1) = D_1 + D_2 + \dots = k_1(\lambda_1)c_1b + k_2(\lambda_1)c_2b + \dots \quad (2a)$$

At another wavelength the extinction coefficients will be different.

$$D(\lambda_2) = k_1(\lambda_2)c_1b + k_2(\lambda_2)c_2b + \dots \quad (2b)$$

Measurement at n wavelengths will therefore lead to n independent equations, in terms of which n components can be expressed.

For the common case of binary mixtures it is more convenient to express the equations in the form

$$c_1 = \frac{k_2(\lambda_2)D(\lambda_1)}{A} - \frac{k_2(\lambda_1)D(\lambda_2)}{A} \quad (3a)$$

$$c_2 = \frac{k_1(\lambda_1)D(\lambda_2)}{A} - \frac{k_1(\lambda_2)D(\lambda_1)}{A} \quad (3b)$$

where $A = [k_1(\lambda_1)k_2(\lambda_2) - k_1(\lambda_2)k_2(\lambda_1)]b$. Because the concentrations are determined as the difference between two measured densities, the error is larger than in the case of no interference. If it is possible to select wavelengths at which the absorption differs considerably, one term in each of Eqs. 3a and b will be much larger than the other, and the accuracy is not much reduced.

In infrared spectrophotometry, by choosing as many frequencies as there are components, a series of linear equations can be set up and solved for the concentrations desired. Under routine conditions a four- or five-component analysis takes about $\frac{1}{2}$ to 1 hr with an accuracy of ± 0.5 to ± 1.5 per cent of total composition for each component.

When the question arises whether more than one absorber is present, owing to contamination, dissociation on dilution, etc., sometimes it is worth while to compare a graph of $\log D$ plotted against wavelength for the sample with the corresponding graph for the pure compound. If the curves for the sample and the reference sample cannot be matched by simple displacement along the $\log D$ axis to correct for the difference in concentration, the compositions are not the same.

It can be shown³⁻⁵ by differentiation of Eq. 1 that, assuming a constant instrumental error in the transmittancy measurement over the total range 0 to 100 per cent, the precision in the determination of concentration is greatest when the transmittancy is between 28 and 36 per cent. The upper figure applies when the error in setting the transmittancy of the pure solvent at 100 per cent is negligible compared with the error in the measurement of the sample transmittancy, and the lower figure applies when the two errors are equal. An exact figure for the optimum transmittancy is difficult to determine because the instrumental error is in general not constant. However, exact values of the transmittancy at which maximum precision is obtained are not especially important because the error in the determination of concentration, which is about three times greater than the error in the transmittancy measurement at the optimum transmittancy, in-

creases very slowly for an appreciable range on each side of the optimum. The concentration error increases rapidly near 0 and 100 per cent transmittancy.

It is impractical to restrict routine practice to measurement in the immediate vicinity of the optimum transmittancy. Extension of the concentration range on each side of the optimum, which is accompanied by an increase in the error, is therefore necessary. The increase in error is less than 20 per cent within the range of approximately 20 to 60 per cent transmittancy; thus a threefold concentration range is covered without appreciable loss of accuracy. Further extension of the range at the expense of accuracy is often necessary, especially in the direction of lower concentrations. It is apparent that the available range depends on the error that can be tolerated.

The maximum sensitivity corresponds to a solution so dilute that its transmittancy can just be distinguished with reasonable certainty from that of the blank, and the error in this case is a factor of 2 in the concentration. Reasonable certainty must still be defined and may be taken as a transmittancy difference twice the standard deviation in the setting of the blank at 100 per cent, in which case there is about one chance in four that the measured transmittancy of the limiting concentration would be equal to that of the blank to within the standard deviation, or it may be taken as a difference of three times the standard deviation, in which case the chance is about one in twenty. Since the standard deviation in the transmittancy measurement with a good spectrophotometer is about 0.1 per cent, the limiting transmittancy is about 99.8 per cent. Sandell has used this figure for quoting sensitivities.

When the interest is primarily directed to measuring the lowest possible weight of a constituent rather than its lowest possible concentration, the analyst can resort to decreasing the final volume of solution. For an established procedure using a definite volume of solution, lower concentrations can be reached if the path length is increased. Equation 1 shows that concentration and cell length are equivalent quantities in the absorption of light. Conventional cells require an increase in volume of solution when the path length is increased. Since path length is the only geometrical factor entering into Eq. 1, reduction of the cross section of the cell is effective in increasing the absolute sensitivity. Capillary cells 5 cm in length and requiring only 0.1 ml of solution have been used successfully and will be described later. Reduction of the cross section means a corresponding reduction in the amount of light available for operating the spectrophotometer; therefore an instrument sensitive to

small quantities of light and adaptable to a variety of cell sizes is required.

Another aspect of Eq. 1 with respect to visual colorimetry should also be mentioned. Null or comparison methods for measuring transmittancy must be used in these instruments because the eye is inaccurate in judging intensity differences, although in some methods, such as in the quinalizarin method for boron, the eye is more sensitive than instruments to changes in hue where there are overlapping absorption bands. It is therefore necessary to provide some means of equalizing the light intensities observed through the sample and comparison solutions in a calibrated manner. This may be accomplished by a provision, such as a diaphragm, polarizer, or wedge, for continuously varying the illumination in one beam. The more common method is to equalize the product of concentration times path length by providing an absorption cell of continuously variable path length. The brightness discrimination of the eye limits the accuracy to approximately 2 per cent.

To summarize, Beer's law is used in practice with photoelectric photometers to obtain straight-line calibration curves of instrument response against concentration. In practice it makes little difference whether transmittancy is plotted on a semilog graph paper or whether optical density is plotted on linear graph paper since a straight line originating at 100 per cent or 0, respectively, is obtained in either case. The choice is partly a matter of convenience although some instruments read only in transmittancy. It must be emphasized that, even when Beer's law is not obeyed, by using calibration curves much valuable information can be obtained with the so-called "filter photometers" in which the band width transmitted by the filters may be considerably wider than the absorption band of the solution being analyzed.

In many instances where interferences occur at the maximum absorption band, measurements may be made at other wavelengths with appropriate calibration curves.

3. SPECTROPHOTOMETRIC ANALYSIS

The analysis of a solution by direct measurement of its absorption spectrum is a common procedure for organic compounds. This method is often less valuable for inorganic compounds because the spectra in general are less distinctive and the colors are less intense. Organic colorimetric reagents are therefore widely used in the spectrophotometric analysis of most metals in solution. Notable excep-

tions are the rare earths, most of which exhibit very characteristic absorption spectra, and the permanganate ion, the absorption of which is comparable in intensity with that of a typical organic reagent. Spectrophotometric methods for uranium in fairly high ranges have been reported, based on the absorption of the uranyl ion.⁶⁻⁸

A different type of analysis for which spectrophotometric methods have been found useful is the determination of oxidation states. The basis for the method can be noted by reference to Fig. 24.1 in which

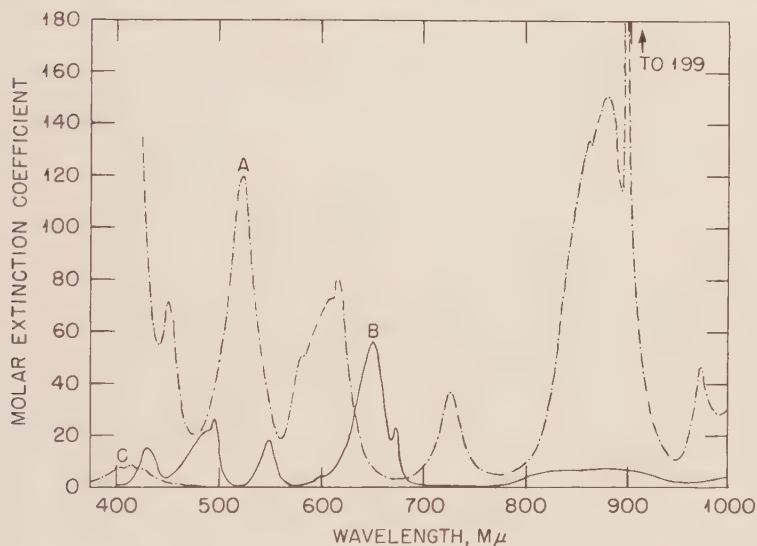


Fig. 24.1—Absorption spectra of uranium. 0.01M uranium solution in 1M HCl. Curve A, uranium(III); curve B, uranium(IV); curve C, uranium(VI). Measurements were made with a Beckman spectrophotometer using 1.75-cm cells.

the molar extinction coefficients for sexivalent, quadrivalent, and trivalent uranium in 1M hydrochloric acid are plotted as a function of wavelength.^{9,10} It will be observed from the numerical values of the coefficients that the spectra are relatively weak; thus high sensitivity, with which spectrophotometric methods are usually associated, is not obtained. On the other hand the spectra are markedly different, and a simultaneous determination of the concentration of each valence state by the standard procedure is quite feasible. The method is applicable to the determination of the oxidation states of neptunium¹² and plutonium¹¹ as shown in Figs. 24.2a and b.

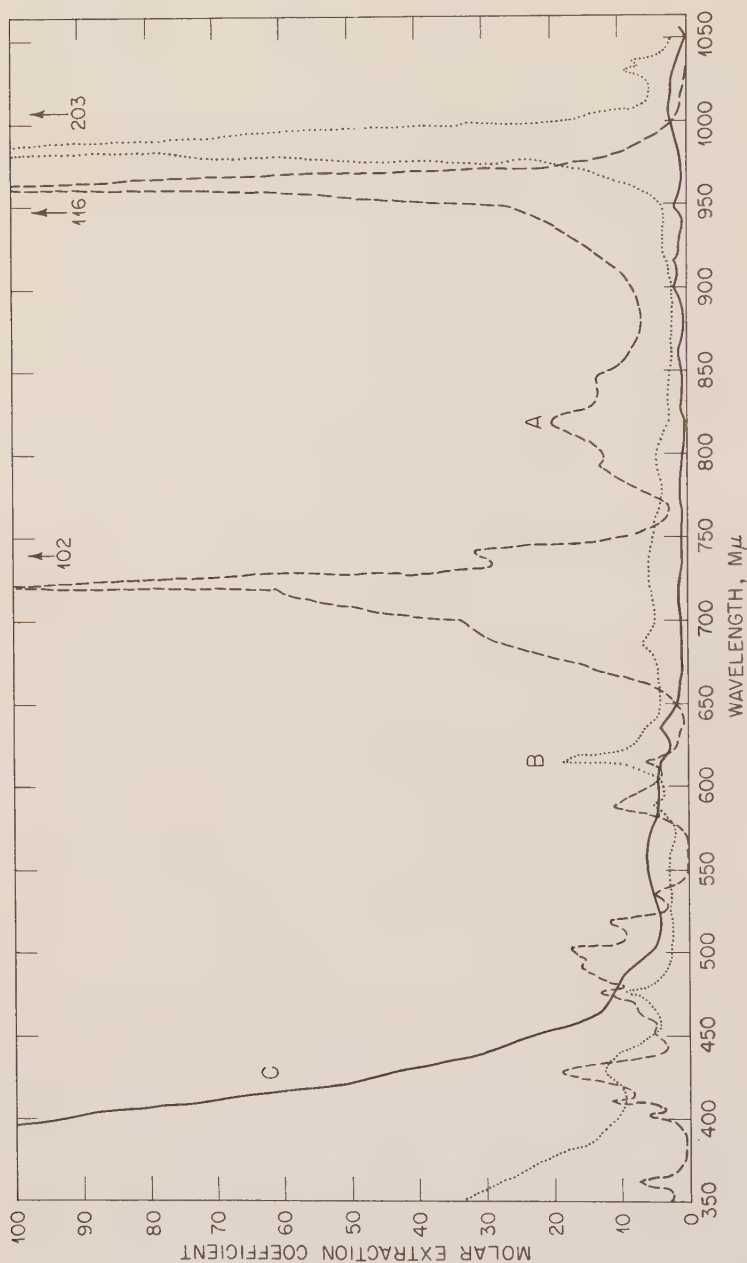


Fig. 24.2a—Absorption spectra of neptunium. Neptunium solutions in 1.0M HCl. Curve A, neptunium(IV); curve B, neptunium(V); curve C, neptunium(VI).

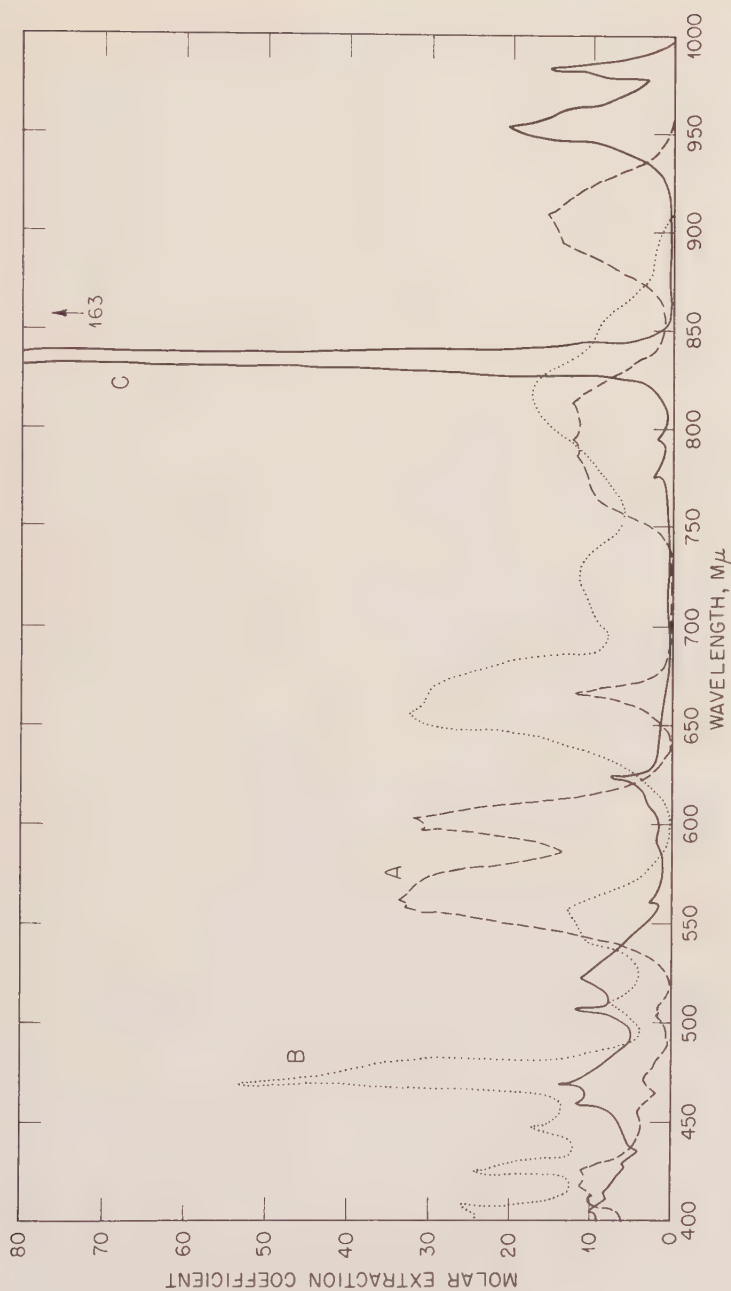


Fig. 24.2b—Absorption spectra of plutonium. Plutonium solutions in 1.0M HClO₄. Curve A, plutonium(III); curve B, plutonium(IV); curve C, plutonium(VI).

4. COLORIMETRIC REAGENTS

The absorption of visible light by a molecule is associated with a change in the electronic configuration, the nature of which determines both the wavelength of the band and its intensity, i.e., the value of the extinction coefficient. Wavelengths and intensities of absorption bands of analytical reagents are largely empirical quantities. Correlation of these data sometimes enables predictions to be made for new reagents by analogy, but the final choice must be based on experiment.

As mentioned in Sec. 3, the absorption spectra of most inorganic ions in solution are not suitable for analytical purposes because they are usually comparatively weak and without distinctive structure. It is common practice in trace analysis to employ colorimetric reagents, usually organic, which react with inorganic ions to form products with much more intense color (see references 3, 13 to 17, and 21). The absorption spectrum of a typical colored complex usually has a peak somewhere in the visible region. Unfortunately, most reagents are selective rather than specific, in that they form complexes with similar absorption spectra for ions of similar size and charge.

The determination of the most suitable reagent for a given type of analysis involves a number of factors such as sensitivity, specificity, interferences due to chemical incompatibilities of other ions under the conditions of the determination, stability, and convenience. Sensitivity is an important consideration, although the question of interferences is usually somewhat more important. A more selective reagent is preferred, in general, to one that is more sensitive but less selective. On the other hand, the latter would be chosen if it were known that no interfering ions were present in the sample, or if they could be removed relatively easily. For best sensitivity, chemical separations are frequently necessary. In some cases a separation can be avoided if the interference is of such a nature that it can be corrected by transmittancy measurements at several wavelengths. The colorimetric reagents used for uranium are considered in Chap. 1, "Uranium."

The variation in kinds of analysis and precision desired throughout the Project was so great that all types of photometers were used.

For control work in many instances, photoelectric filter photometers were exceptionally useful because of their ease of operation and freedom from instrumental troubles. With these instruments, filters were used to select the band desired. In many cases Beer's law was followed by using these instruments, and when this was not the case, calibration curves using standard solutions sufficed. At one

site or another nearly all commercial photoelectric filter photometers on the market were used. In certain installations where the line-voltage variation was excessive, one-cell instruments run off the 120-volt a-c line were unsatisfactory. In many of these cases the two-cell balanced-circuit instruments were satisfactory.

For certain types of work it was found desirable to use photoelectric spectrophotometers, and in the research installations they were used extensively.

5. INFRARED SPECTROSCOPY¹⁸

Infrared spectroscopy is based on the fact that molecules have certain fixed or characteristic vibrational frequencies. The values of these frequencies lie in the infrared range of the electromagnetic spectrum. They are determined by the mass of the atoms involved, their spatial configuration, and the interatomic forces binding the atoms. In the general case of a molecule of n atoms there will be $3n - 6$ of these "normal" or characteristic frequencies.

If the motion of the atoms in one of these frequencies results in a change of the dipole moment of the molecule, infrared radiation of the same frequency as that incident on the material will be absorbed. The infrared spectrum of a material is obtained by irradiating the sample with a continuous source of infrared radiation, by dispersing this radiation, and measuring the percentage transmitted by the sample at each frequency.

The range of these fundamental vibrations is from 4000 cm^{-1} ($2.5\text{ }\mu$) to 100 cm^{-1} ($100\text{ }\mu$), although the range generally studied today is limited to 400 cm^{-1} ($25\text{ }\mu$) by the sources and dispersing mediums available.

Barring cases of strong intermolecular action such as chemical reaction or hydrogen bonding, the spectrum of a mixture of materials is the superposition of the individual spectra of the components in the proportion in which they are present. Hence, the basis of analysis of a given mixture is to obtain the spectrum of each component in its pure state, choose for each component a strong absorption frequency at which the other components have a weak or negligible absorption, and correlate the absorption at this frequency with the concentration of this component in the mixture.

One or two features of infrared spectroscopic analysis might be pointed out. Since absorption is a logarithmic function of concentration, the accuracy based on total composition is best in low-component concentrations. Thus in obtaining and setting up specifications on a pure material the infrared spectrum may be used to trace the success

of various purification methods by following the disappearance of the strong impurity bands. The final purity may be determined by a very accurate measurement (approximately ± 0.1 to ± 0.01 per cent) of the impurities and a determination of the major component by difference.

6. INSTRUMENTS FOR PHOTOMETRIC MEASUREMENT

6.1 Visible and Ultraviolet Region. The characteristics desirable in a spectrophotometer include the following: maximum accuracy in the transmittancy measurements; stability with time in the transmittancy measurement system; reproducibility in setting the wavelength interval and mean wavelength used; minimum wavelength interval (effective slit width) required for 100 per cent transmission; maximum wavelength range accessible; flexibility in accommodations for cells of various shapes and sizes; maximum spectrum purity (freedom from scattered light, etc.); convenience, speed, and simplicity of operation; minimum maintenance; and maximum compactness of construction. The type of spectrophotometer employed depended to a great extent on the use to which it was to be put. Since transmittancy curves are an integral part of colorimetry, it was necessary to examine many solutions and glasses. For obtaining transmission curves of certain solutions and glasses the General Electric recording spectrophotometer was ideal. A brief description of the instrument used follows.

The General Electric spectrophotometer consists essentially of a Van Cittert-type double monochromator with prismatic dispersion and an electrically operated polarization photometer. In use there is an alternating illumination of the standard and the unknown which produces a flicker effect in the integrating sphere. The photocell serves merely as a null-point indicator. Wherever the two light beams are of unequal intensity, the photocell actuates a balance motor that rotates a Rochon prism until equality of illumination is achieved. For any given setting of the wavelength scale the transmittancy (or reflectance) may be read on the photometer scale. Since both standard and unknown are under illumination, the value is obtained directly. When using the recorder the operator has only to see that the instrument is in adjustment, place the sample in position, and start the motor operating the wavelength cam. The curve is plotted automatically. Different cams may be used to obtain curves having the desired ordinate and abscissa scales. The wavelength range is 400 to 750 $m\mu$.

The Beckman monochromator utilizes a 30-deg quartz prism in a Littrow mount with a spherical mirror instead of a lens. Both the en-

trance and exit slits are continuously adjustable in width. The wavelength range of 210 to 1200 $m\mu$ is obtained by the appropriate combination of light source (tungsten or hydrogen), filter, and photocell. The amplified output of the photocell is balanced against a slide-wire potentiometer that has a scale reading in both transmission and density units. A notable convenience is a means of switching out the potentiometer for balancing the transmittancy of the blank at 100 per cent without having to set the dial at 100.

The Coleman model 10S is a double monochromator using replica transmission gratings. A special potentiometer or a Coleman pH meter is required as an accessory to measure the photocell output. It is read directly in transmittancy units, but no direct density scale is provided. Interchangeable fixed slits giving bands (with preference for the 5- $m\mu$ band) of 5, 7.5, 15, and 30 $m\mu$ effective width are available, and the wavelength range is 350 to 1000 $m\mu$.

The Coleman model 11 is a single monochromator also using a transmission grating. The slit is fixed at an effective width of 35 $m\mu$, and the wavelength range is about the same as for the Coleman model 10S. Measurements are made using either deflections of a built-in galvanometer reading directly in transmittancy or by a null method against a wire-wound potentiometer reading in both transmittancy and optical density. It has proved useful for routine work when used in conjunction with filters to reduce scattered light.

Transmittancy curves were obtained using both the Coleman model 10S with 5- $m\mu$ band width and the Beckman quartz spectrophotometer. The Coleman model 10S, 5- $m\mu$ slit, has the advantage of constant dispersion with a uniform band width throughout the range 350 to 1000 $m\mu$ but has no flexibility in accommodation for cells of various shapes and sizes. The Beckman spectrophotometer has flexibility for accommodation of cells of various sizes, but the dispersion changes with wavelength and necessitates constant adjustment of slit width if constant band width is desired.

The photoelectric filter photometers mentioned are so well known that a detailed description is unnecessary. Essentially the light band is isolated by filters, and the radiant energy is measured by a photocell after passing through the solution in question.

The usual Duboscq-type colorimeters have been used as well as ordinary Nessler tubes. In some laboratories considerable use has been made of the Lovibond tintometer.

Of particular interest in the analytical work reported has been the attempt to increase the absolute sensitivity of spectrophotometric methods by reduction of the volume of solution required. This development has been greatly facilitated by the fact that the Beckman spec-

trophotometer has sufficient light sensitivity in the visible region so that absorption cells with cross-sectional areas much smaller than those normally supplied can be used with full-scale reading for the blank.

The standard 1-cm square cell supplied with this spectrophotometer requires 2.5 to 3 ml of solution to cover the beam emerging from the monochromator. The most convenient modification, which enables 1 ml to be measured, consists in utilizing the solution normally under the beam in the conventional arrangement by raising the cell $15/32$ in. This is accomplished by inserting a small block in the bottom of the cell holder as shown in Fig. 24.3. The block should have a lip extending up $1/16$ in. on the edge next to the slit in order to screen the bottom of the cell and a notch on the bottom facing the spring in the cell holder. The volume can be further reduced at the expense of inconvenience in use by inserting pieces of glass inside the cell at its sides. When the cell is used in this way, the exit slit should be covered by a mask with a smaller opening.

This adaptation has been further extended by fabricating capillary absorption cells with a light path as long as 5 cm.¹⁹ A suitable cell design shown in Fig. 24.4 consists of a plastic body with threaded end caps for supporting the replaceable windows. The bore of the capillary is drilled and reamed in a lathe in a suitable length of $5/8$ -in. round rod. It was found that an external shape other than round was desirable for reproducible orientation in the spectrophotometer because a slight displacement of the axis of the cell is more serious than in conventional cells. Filling is accomplished by means of small holes drilled through the wall near each window; the optimum size and distance from the windows vary with the size of the bore. The most suitable plastic for machinability and chemical inertness was found to be Du Pont's D-25, which resembles a casein plastic in opaqueness and therefore serves to define the area of the beam. Internal reflections, at least from a plastic of this sort, do not seem to be a disturbing factor.

Two sizes were adopted, one with a bore of 2 mm and the other of 4 mm, each with a 5-cm length, the volumes being 0.16 and 0.65 ml, respectively. The absolute sensitivities obtained were related exactly in the ratio of volumes of solution required.

A spectrophotometer cell was developed for use with the Beckman instrument whereby a solution could be electrolytically reduced *in situ*.⁴⁶ The reduction cell employed consists of a 1-cm Corex spectrophotometer absorption cell with airtight connections (Fig. 24.5). The complete electrolytic apparatus was mounted in a Beckman spectrophotometer 1-cm cell holder for convenient transfer to the spectro-

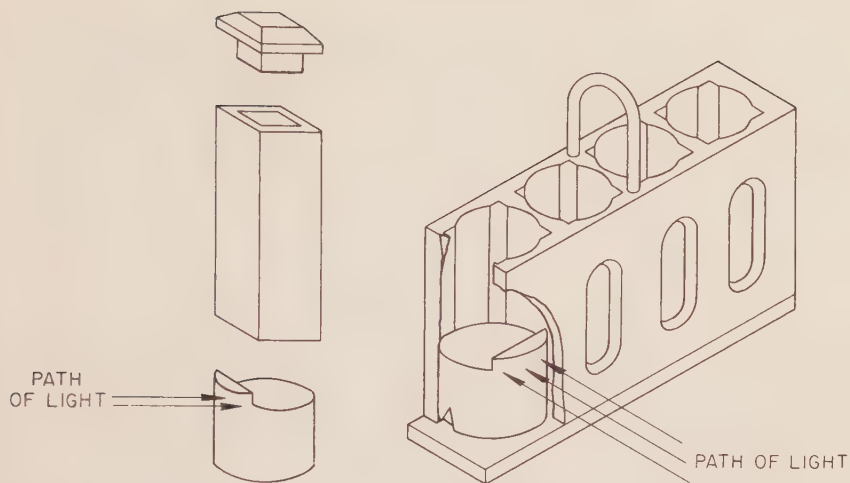


Fig. 24.3 — Block for use with Beckman cell holder.



Fig. 24.4 — Capillary absorption cell.

photometer. Cells A and B are 1-cm absorption cells to which cylindrical glass threaded tops of 1 cm inside diameter were fastened with deKhotinsky cement. Cell A is the spectrophotometer blank containing dilute hydrochloric acid. Evaporation was prevented by a screw cap.

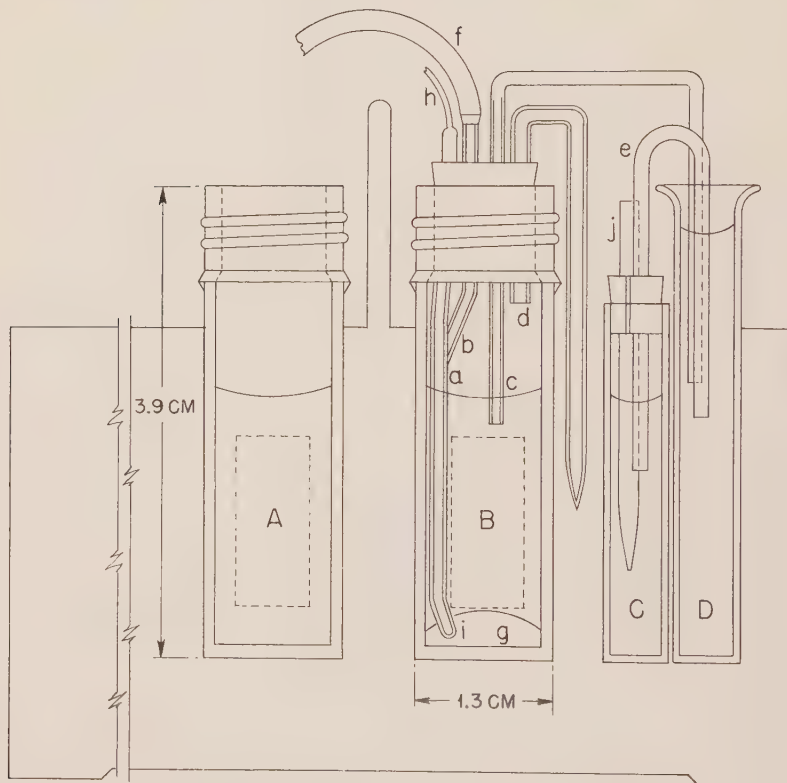


Fig. 24.5—Spectrophotometer electroreduction cell.¹⁶

Cell B is the reduction cell, which was closed by a small cork. Glass capillaries of 1 mm inside diameter are marked a, b, c, d, and e; a is filled with mercury to make electrical contact with a copper-strand lead, h, and a platinum wire in the tip i, which in turn contacts the mercury-pool cathode g; b is a nitrogen inlet, the tip of which (not shown) projects down into the solution; f is a short section of flexible plastic tubing for connection to a nitrogen supply; c is a saturated KCl-agar bridge; d is a vent, the tip of which extends outside below the solution level to prevent escape of the hydrogen-nitrogen blanket over the solution. All tubes in cell B were sealed into the cork with

deKhotinsky cement. Cell D contains saturated KCl and is the central compartment for agar-bridge connections. The potential of the solution in cell B was measured by inserting a saturated KCl-agar bridge connected to an exterior calomel electrode (not shown) into cell D and making connection through the copper lead h. Cell C is the anode compartment containing dilute hydrochloric acid and is connected to cell D by the agar bridge e. The graphite anode j is a section of 2-mm soft pencil lead. A slit in the cork serves as a chlorine vent.

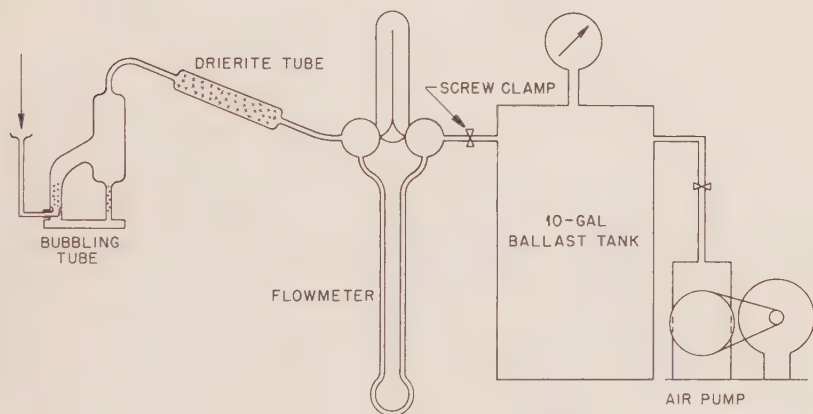


Fig. 24.6—Gas-sampling system. (Courtesy of The Kellex Corporation.)

The spectrophotometer cell holder is shown in outline. The approximate area of the slit apertures is indicated by the dashed rectangles in the absorption cells. A strip of ruled graph paper (not shown) attached to the back of cell B and above the slit aperture was calibrated as a volume indicator.

An instrument for the continuous sampling and colorimetric analysis of traces of fluorine-containing gases, such as HF, in air in conjunction with the Ferrisal reagent,²⁰ whereby the reagent is bleached by fluoride ion, is described by Greenspan and Stein. The unit consists of a balanced-type photoelectric bridge circuit, containing a common light source and two photocells and is shown in Fig. 24.9. Two specially designed absorption cells each containing the colorimetric reagent are used. Air containing traces of the impurity of interest is continuously circulated through one of the cells. The resultant color change throws the bridge off balance, actuating a meter or alarm.

Figure 24.6 is a schematic diagram of the gas-sampling system. The flow rate was selected to be 1 liter per minute. The "bubbling tube" of Fig. 24.6 schematically represents two absorption cells, the "analyzer" cell and the "standard" cell. The contaminated air is

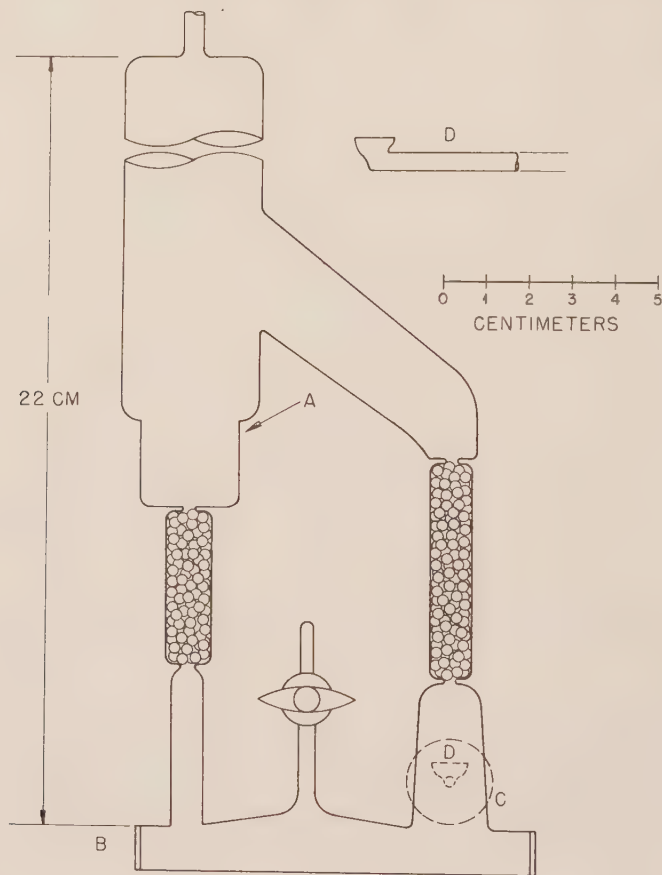


Fig. 24.7—Continuous-circulation absorption cell. A, level of colorimetric reagent; B, pyrex optical flat; C, flare for No. 1 stopper; D, gas disperser. (Courtesy of The Kellex Corporation.)

sent through the analyzer cell, and "pure" air is obtained from a known pure source (next room, outside air, tank, etc., or by chemically pretreating the room air before it enters the standard cell). The object of using two cells in this differential manner is to minimize the effect of evaporation errors, temperature changes, and line-voltage fluctuations.

Figure 24.7 represents one of the types of continuous-circulation absorption cells. The cell operates on an automatic-lift-pump principle. The colorimetric reagent is added to level A (Fig. 24.7). The air is introduced through a rubber-connected glass-inlet jet tube (lower part of right leg, Fig. 24.7) provided with a perforated bubble disk at its mouth. If the dust content of the air is low, a fritted-glass

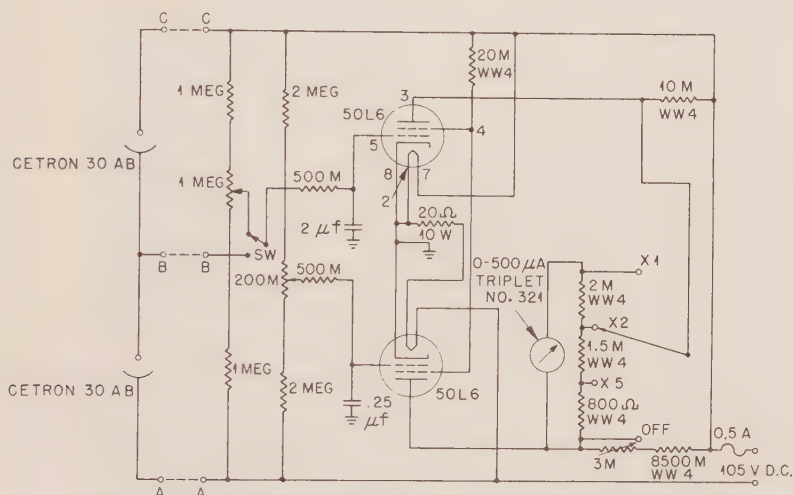


Fig. 24.8—Circuit diagram of amplifier used with continuous-circulation absorption cells. (Courtesy of The Kellex Corporation.)

disk is preferable since it gives better gas dispersion. A column of glass beads in the mixing leg (right leg, Fig. 24.7) of the cell aids in efficient removal of the gas contaminants. The entering air pushes a portion of the liquid over the lip of the cell into the return leg (left leg), while the washed air is pulled out through the top of the bubbler. The column of glass beads in the return arm filters out entrained gas bubbles and allows the liquid to seep through into the "optical" portion of the cell. Thus there is continuous circulation of liquid through the cell. The stopcock is used in removing reagent from the cells and also in adjusting the volume of reagent in the cell. The sloping construction leading to the stopcock serves to remove and store any air bubbles that do come through and therefore to remove them from the light path.

The light source is a 120-volt Mazda 100-watt projection lamp, No. 100T8/108SC, with bayonet base. The lamp is mounted on an adjustable stand in a ventilated metal housing with a large hinged door

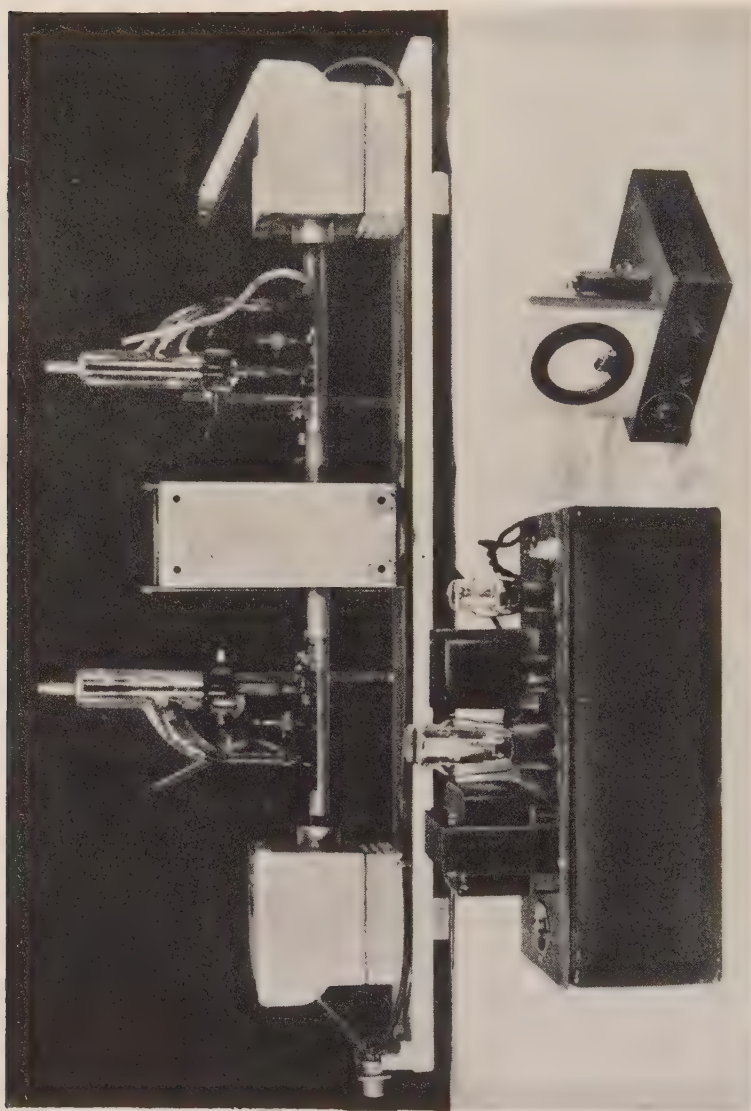


Fig. 24.9—Photometric colorimeter for analysis of continuous flowing gas stream.
(Courtesy of The Kellex Corporation.)

for easy access. Light from the lamp passes through two holes in opposite sides of the lamp housing, then through convex lenses set in modified buret meniscus readers. After passing through the reagent solution the light is sent through an iris diaphragm to a gas-filled phototube. The diaphragms are used to equalize the amount of light reaching the two opposing phototubes and to reduce the effects of stray light. The phototubes are mounted in sheet-metal boxes with hinged covers.

Figure 24.8 is a diagram of the amplifier. The phototubes are mounted in a balanced Wheatstone-bridge arrangement with the two amplifying tubes. Any change in light intensity of the test-cell solution affects the grid and thus the plate current on one of the 50L6 tubes. A microammeter placed across the two plates indicates the change in current. The meter deflections are calibrated in concentration terms by comparing a series of varying deflections with those obtained with the same solutions on a standard colorimeter. The complete instrument is shown in Fig. 24.9.

6.2 Infrared Region. The Perkin-Elmer model 12 infrared spectrophotometer was used extensively on the Project. This is shown schematically in Fig. 24.10. Continuous infrared radiation from the source G is focused by the mirror M2 on the entrance slit S1. The beam from S1 is collimated by M3, refracted by the prism P, returned, and directed by the mirror M5 on to the exit slit S2. The radiation from S2 is focused by M7 on to a compensated vacuum thermocouple Tc. The electrical output of Tc is led to an amplifying system and recorder.

An infrared analyzer was developed¹⁸ for measuring the concentration of fluorocarbon vapors in air. The gas analyzer consists of a source of infrared radiation, two identical optical systems for sample and dummy cells, and a detector for measuring the differences in the amounts of radiation transmitted by the two cells. The instrument is made selective to fluorocarbon vapors by using a detector, based on the gas-thermometer principle, filled with a mixture of fluorocarbon vapor and nitrogen. The deflections of the oil drop in a capillary connecting two chambers of the gas thermometer are measured by utilizing the fact that the presence of the drop in the capillary forms a lens system, which will focus a sharp image of a filament lamp on a slit in front of a photocell. The deflections of the drop throw more or less light on the cell, the output of which is measured with a galvanometer or automatic recorder.

The optical system of the gas analyzer is shown in Fig. 24.11. The Globar source at 200 watts gives approximately the same radiation

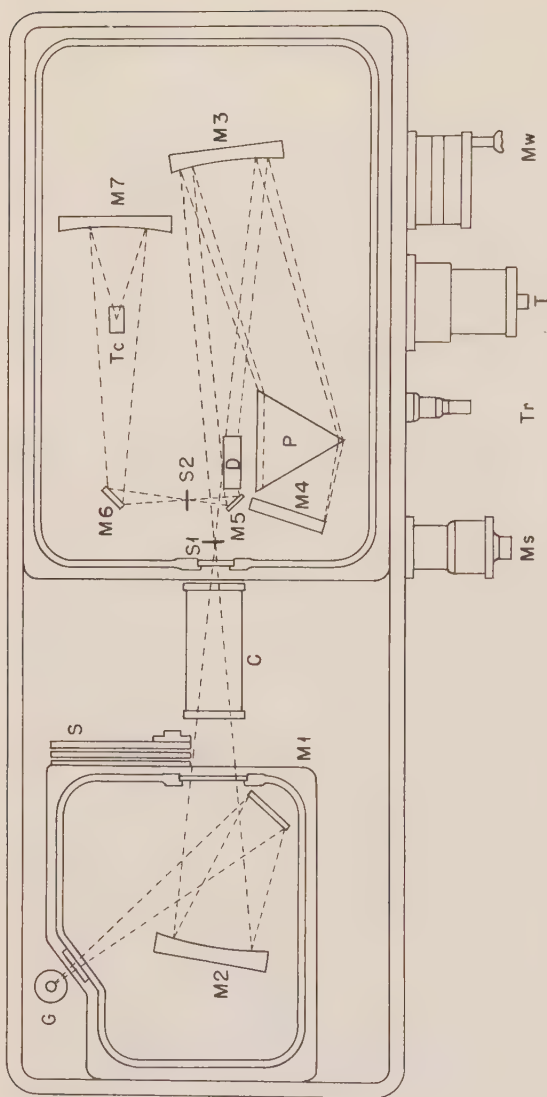
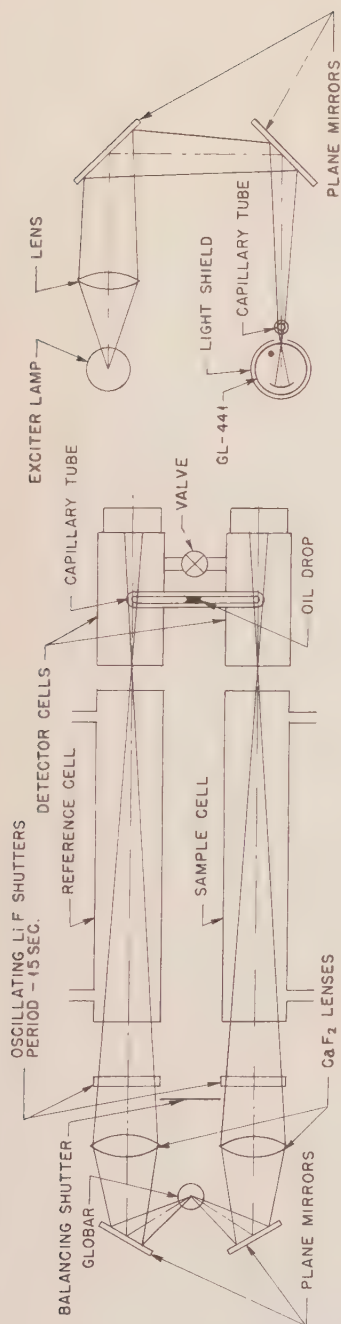
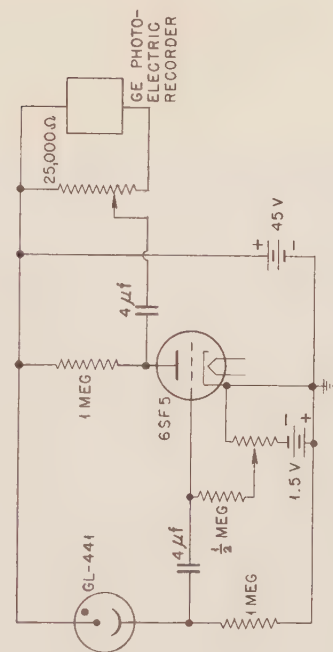


Fig. 24.10—Perkin-Elmer model 12A infrared spectrophotometer. (Courtesy of the Perkin-Elmer Corp.)

- | | |
|------------------------------|----------------------------|
| C, sample cell | P, prism |
| G, globar source | S, shutters |
| M1, M4, M5, M6, flat mirrors | S1, entrance slit |
| M2, M7, spherical mirrors | S2, exit slit |
| M3, off-axis paraboloid | T, turret drum |
| Ms, slit micrometer | Tr, turret release |
| Mw, wavelength micrometer | Tc, thermocouple |
| | D, temperature compensator |



B. PHOTOCELL-EXCITER LAMP OPTICAL SYSTEM



D. PHOTOCELL CIRCUIT WITH RECORDER

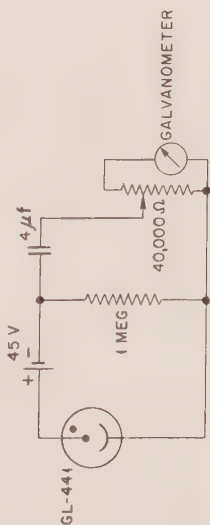


Fig. 24.11—Schematic diagram of gas analyzer. (Courtesy of the Stanford Research Laboratories, American Cyanamid Company.)

as a black body at 900°C . The radiation is focused through the sample and reference cells and through the detector chambers by CaF_2 lenses, which limit the beams to wavelengths shorter than 11μ . (See Fig. 24.12 for the transmissions of CaF_2 , LiF , and C_8F_{16} in the region

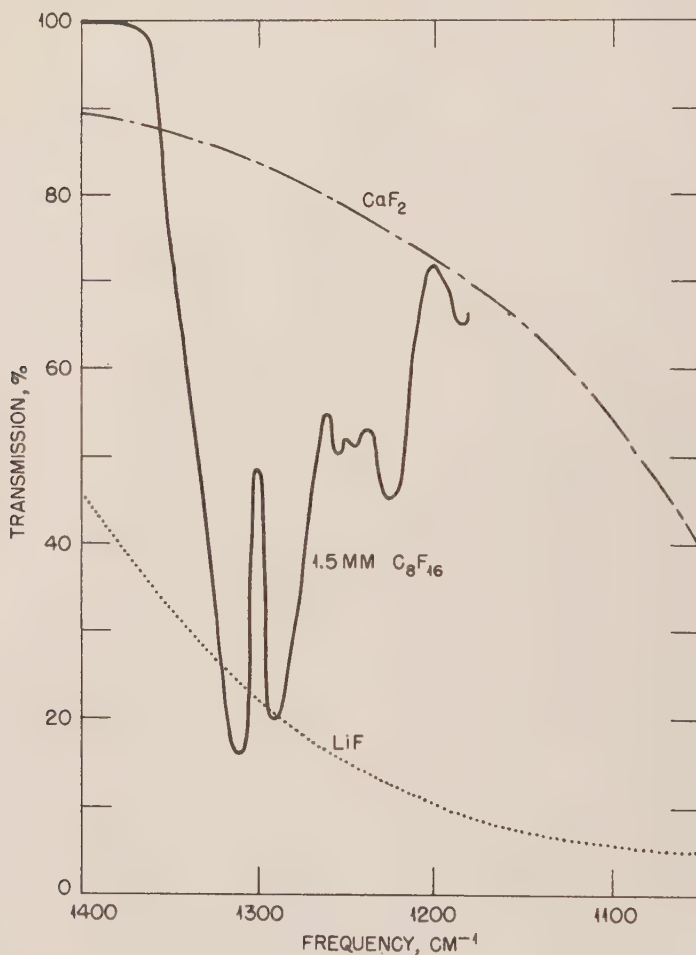


Fig. 24.12—Transmission of CaF_2 , LiF , and C_8F_{16} . (Courtesy of the Stamford Research Laboratories, American Cyanamid Company.)

of interest.) The LiF shutters (Fig. 24.13, H, H') oscillating at four cycles per minute flicker the radiation beyond 7μ and leave the radiation below 7μ continually transmitted. This combination limits the alternating portion of the beams to the wavelengths between 7 and 11μ .

The detector, Fig. 24.14, consists of two chambers with polystyrene-coated rock-salt windows and filled with fluorocarbon (1,3- + 1,4-perfluorodimethylcyclohexane) to absorb radiation corresponding to the C-F stretching vibrations. These two chambers are connected

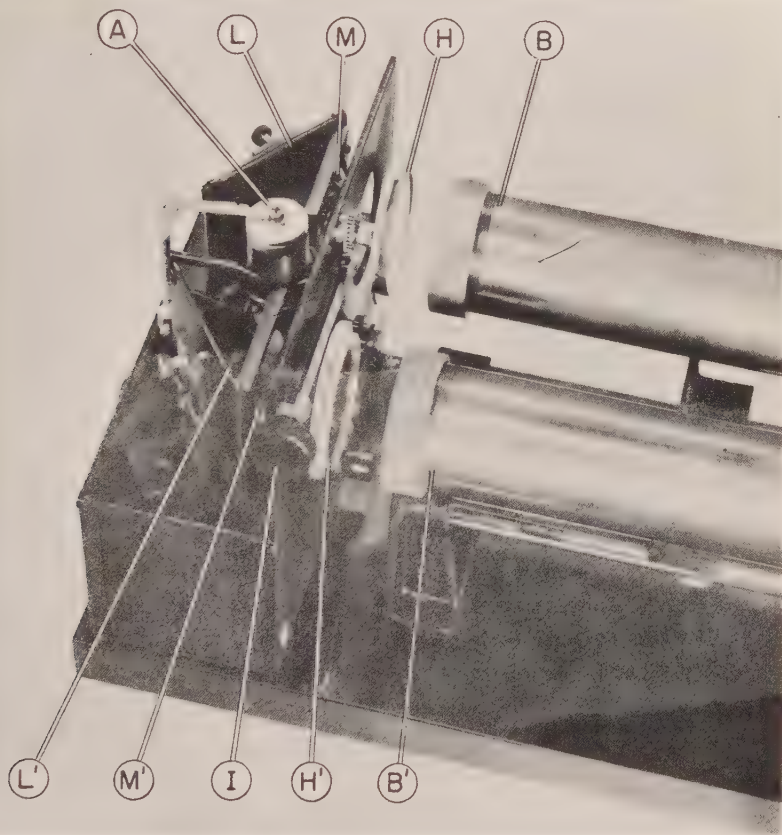


Fig. 24.13—Shutter system for gas analysis. A, source housing; B, B', absorption cells; H, H', shutters (LiF); I, balance shutter control; L, L', plane mirrors; M, M', fluoride lenses. (Courtesy of the Stamford Research Laboratories, American Cyanamid Company.)

by a 2-mm I.D. capillary tube containing a drop of Deobase oil. As shown in Fig. 24.11B the capillary drop in the tube forms a lens system, which focuses an image of the exciter lamp filament on a slit in front of a photoelectric cell. A change in the relative amounts of radiation absorbed by the two detector chambers such as that produced



Fig. 24.14—Detector for gas analyzer. D, control for stopcock connecting detector cells; E, capillary tube controlling oil (Deobase) drop; F, exciter lamp; F', adjustable base for exciter lamp; G, photocell housing; J, J', leveling screws for detector unit; K, clamping screw for detector unit; N, lens for focusing image of exciter-lamp filament on capillary tube; O, housing for two-plane mirrors (part of photocell-exciter optical system); R, clamp for ground joint. (Courtesy of the Stamford Research Laboratories, American Cyanamid Company.)

when a sample is placed in one beam results in a change in the temperature differential between the two cells, and the oil drop moves to equalize the corresponding change in pressure. Approximately half the length of the image of the exciter lamp is masked off in order that when the drop moves, more or less light will fall on the phototube. The alternating-current output of the tube is measured with a galvanometer or recorder in conjunction with suitable electrical circuits (Fig. 24.11). The four-cycle-per-minute frequency is so low that no attempt has been made to rectify the signal to direct current. The rate of change of signal is slow enough that no difficulty is experienced in reading the end point of each deflection.

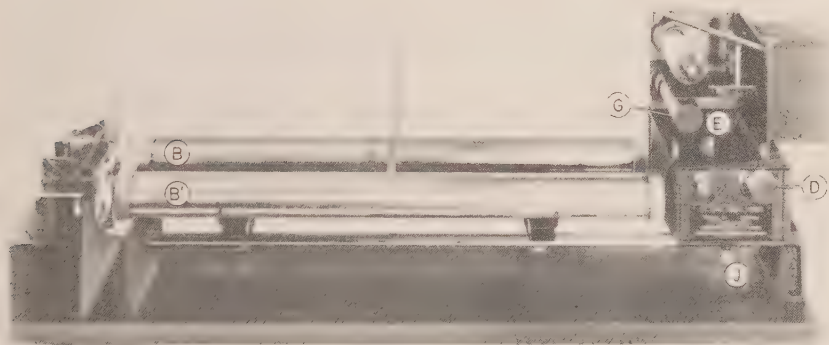


Fig. 24.15—Complete gas analyzer. Letter designations of parts correspond to those used in Figs. 24.13 and 24.14. (Courtesy of the Stamford Research Laboratories, American Cyanamid Company.)

The size of the detector makes it difficult to maintain the ambient temperature of the two chambers exactly the same. Variations in these temperatures cause the oil drop to drift to one side or the other of the capillary. In addition, variations in the bore of the capillary tubing make the results depend on the position of the oil drop in the tube. These troubles were solved partly by opening a stopcock by-passing the capillary tube, thus allowing the oil drop to settle into the low portion in the center before each reading. Later a small permanent by-pass was introduced to keep the drop near the center of the tube without need of manipulation of the stopcock by the operator.

The absorption cells used for the determination of C_8F_{16} in air were 60-cm brass cells with rock-salt glyptal-sealed windows.

The source, cells, and detector were mounted separately on ways to permit the use of absorption cells of various length or additional detectors for multicomponent work. A photograph of the completed instrument is shown in Fig. 24.15.

The gas analyzer will detect about 5 ppm of C_8F_{16} vapor in air and will measure concentrations greater than 100 ppm with an accuracy of ± 5 per cent. For concentrations greater than 500 ppm a shorter cell had to be used. Baird Associates²² have recently placed a different type of infrared analyzer on the market.

7. NEPHELOMETRIC AND TURBIDIMETRIC METHODS

Inasmuch as no significant developments have been undertaken on the Project on analytical methods that depend on light scattering by colloidal precipitates, this subject is not treated with any detail. These methods, which are standard for such determinations as small amounts of chloride or silver as silver chloride and of sulfate as barium sulfate, are described in standard reference books.^{3,23} Nephelometry and turbidimetry differ in this way: In the nephelometric method the illumination of the sample is at a right angle to the line of sight so that the light scattered by the precipitate is observed, whereas in the turbidimetric method the illumination is along the line of sight as in colorimetry.

Nephelometric procedures are considered to be more sensitive than turbidimetric. Both require empirical calibration and suffer from the fact that light scattering depends on particle size as well as concentration; therefore the results are sensitive to variations in the procedure. For some applications, however, they are adequate.

The conventional turbidimeter is simply a visual colorimeter with opaque cell walls to avoid nephelometric effects. It has been found²⁴ that a spectrophotometer can be substituted with some gain in precision and sensitivity. A wavelength setting in the near ultraviolet is used because the light scattering is proportional to λ^{-4} .

Several types of nephelometers have been used at various Project sites. One, conventional in design, is operated on the variable-depth principle commonly used in colorimeters. Another instrument used, which was manufactured by Hellige, Inc., is based on an unusual method of measurement in that only one cell of fixed depth is used; the relative illumination from the outer and central regions is equalized by matching an annular split field.

The Coleman nephelometer attachment for the Coleman model 11 spectrophotometer has also been used. In this instrument, approximately monochromatic light is used to form the Tyndall beam. The

scattered light is measured by two photocells at right angles to the Tyndall beam.

8. FLUOROMETRIC METHODS

Analytical procedures based on fluorescence have been the subject of rather intensive study. Most of this work has been related to two specific applications—the determination of traces of uranium by means of the fluorescence of the uranyl ion (see Chap. 1) and the determination of traces of fluorine by quenching of the fluorescence of the aluminum-morin complex (see Chap. 5). Some miscellaneous applications, such as the detection of traces of centrifuge oil in aqueous solutions²⁵ and the determination of porphyrins, have also been made.

Uranyl fluorescence provides a method for the determination of uranium which is more sensitive by a considerable factor than any other method known.

For a number of years the fluorescence of fluoride salts in the presence of uranium has been used as a sensitive test for the detection of minute amounts of uranium.²⁶⁻²⁹ The method has been used at various Project sites for the determination of uranium.³⁰⁻³⁸ The fluorescence extends from the blue to the red with maximum intensity in the green, and the spectra are independent of the wavelength of the exciting light as long as the latter is of shorter wavelength than the fluorescence. The over-all intensity, however, increases if the exciting light falls in a region of stronger absorption. The fluorescence spectrum has an envelope of broad maxima with a spacing of about 830 cm^{-1} . As many as eight of these bands are visible if the intensity is great enough. The positions of the maxima are very similar for all uranyl compounds except when the uranium has been fused with sodium fluoride; in this case the entire spectrum is shifted so that the band with maximum intensity falls in the yellow instead of the green. Within each band finer structure can be observed. Some uranyl compounds show more structure than others. If the sample is not a glass, the resolution of this structure is increased by cooling to liquid-air temperature.

The intensity of the fluorescence in crystalline compounds and in solution is also increased by cooling. The greatest intensity, however, is obtained if the sample is prepared by fusing in sodium fluoride or a fluoride-carbonate mixture (see Chap. 1), in which case cooling is without effect.

The intensity of the fluorescence is proportional to the intensity of the exciting light.

8.1 Fluorometers. There have been several types of fluorometers recommended, ranging from the single adaptation of a Duboscq colorimeter (see references 30, 34, 39, 40) to the elaborate instrument of Price.³³ In several installations³⁴ visual estimation has been used.

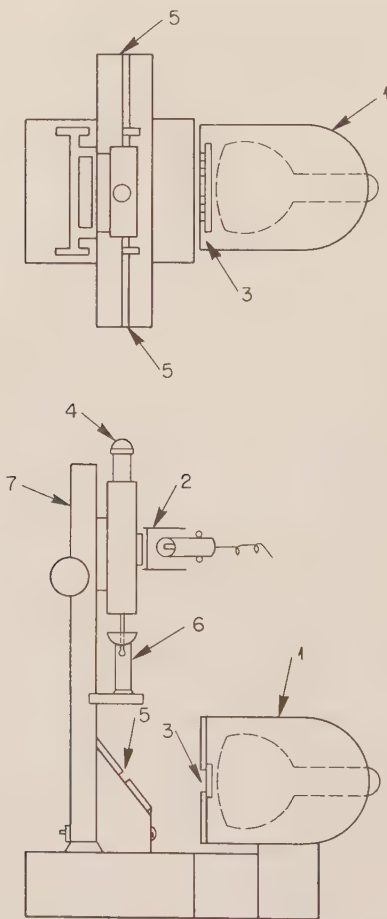


Fig. 24.16—Schematic drawing of visual fluorometer. 1, CH-4 lamp and housing; 2, neon-glow bulb to illuminate scale; 3, slits and Corning No. 586 or 587 filters; 4, Wratten G unmounted gelatin filter in eyepiece; 5, slots to accommodate beads; 6, dye solution in cup; 7, colorimeter with 25- or 50-mm range.

A simple instrument^{30,34,40} for obtaining a quantitative measurement of the relative intensity of fluorescence of two beads was constructed from a Duboscq colorimeter and a small mercury-vapor lamp with a purple filter. As can be seen in Fig. 24.16 the ultraviolet

lamp is so placed that the light shines on the beads. Each bead is placed under a cylindrical prism of the colorimeter, and the path of the fluorescent radiation leads through an absorbing medium before reaching the cylindrical prism. In these experiments methylene blue³⁰ and copper sulfate³⁴ were used as the absorbing medium. Later work⁴⁰ indicated that a solution of a monocarbazyl dye was more effective than methylene blue. A similar instrument employing 5 per cent copper sulfate as a variable filter has also been used.³⁴ An India-ink solution was also employed.

A commercial fluorometer such as that made by the Klett Mfg. Co. was used for the determination of small amounts of fluoride ion.⁴¹ In the Klett model 2070 the sample is compared directly with a standard and is independent of fluctuations in the intensity of the exciting light.

An instrument⁴² that in various modifications is similar in principle to one designed by Neuman^{43,44} is shown in Fig. 24.17. These instruments are simple to construct, are relatively inexpensive, and except for very low amounts of uranium have proved as valuable as any of the fluorometers used. The instrument⁴¹ consists of a portable photometer (Photovolt model 512) and a box for the fluorescence measurement. The fluorescent disk is held (horizontally) at the bottom of a lighttight box, the search unit of the photometer is held directly over the disk, and the incident ultraviolet light strikes the disk from the side at an angle of 45 deg. The bottom of the box holds a slide having depressions to hold five disks which may be brought successively under the photocell. The fluorescence chamber is a block of wood drilled vertically for the fluorescent light and at 45 deg for the incident light. This block is covered in turn by a box that reduces stray light and also provides a support for the photometer search unit and for the ultraviolet lamp.

The ultraviolet source is a Hanovia Chemical & Mfg. Co. type 16200 lamp provided with a transformer to operate on 100-volt alternating current. The incident light passes through an ultraviolet filter (transmitting mainly at 366 $m\mu$); the fluorescent light emitted passes through a yellow (Corning No. 3486) and a blue (Corning No. 9780) filter. The blue filter must be between the photocell and the yellow filter, which may fluoresce slightly. A shutter is used to shut off the ultraviolet light, and a screen passing 10 per cent of the light is also incorporated for use with high-concentration samples. The depressions in the slide are 2 in. square and will accommodate dishes of that size or smaller dishes with suitable adapters.

The dishes used are made of gold sheet, are held in holders, and are fused as shown in Fig. 24.18. The die used for the dishes is also shown.

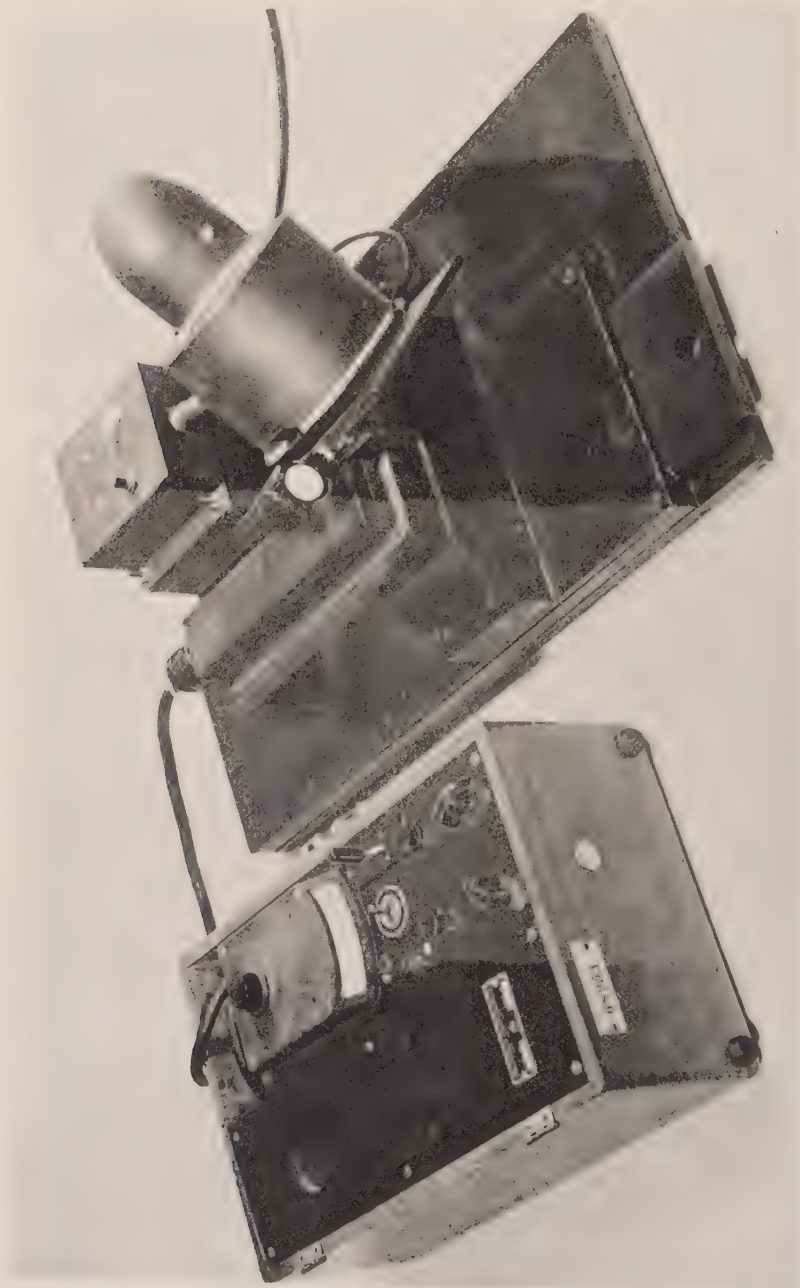


Fig. 24.17—Photoelectric fluorometer.

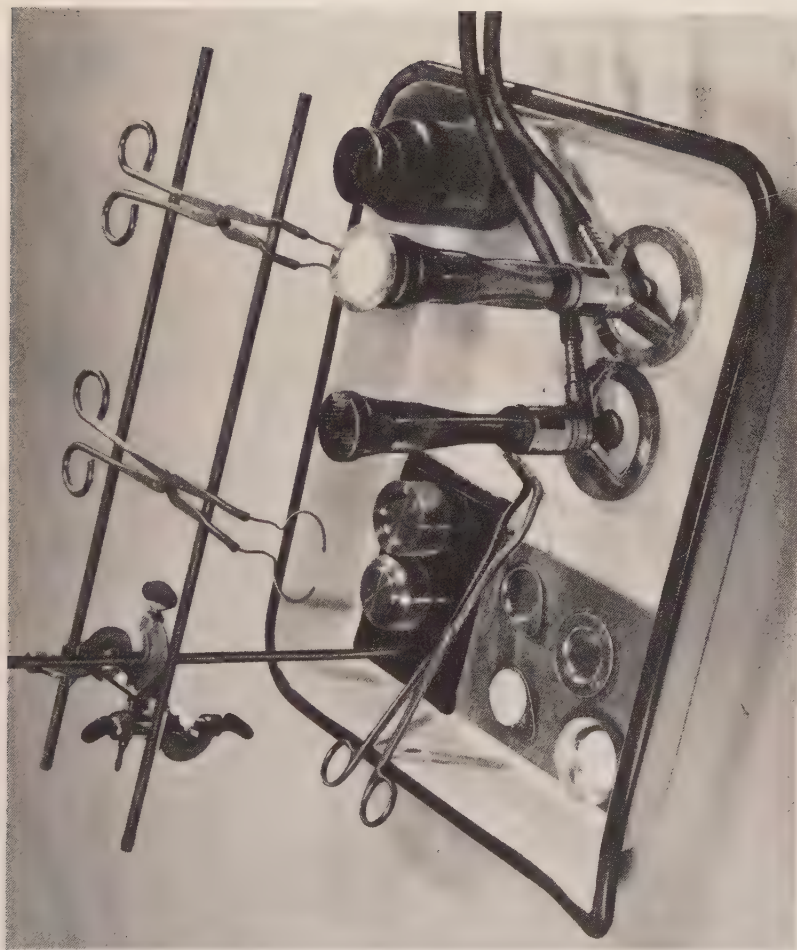


Fig. 24.18—Fusion assembly for use with the photoelectric fluorometer.

The apparatus of Neuman is described in detail in "The Pharmacology and Toxicology of Uranium Compounds," National Nuclear Energy Series, Division VI, Volume 1.

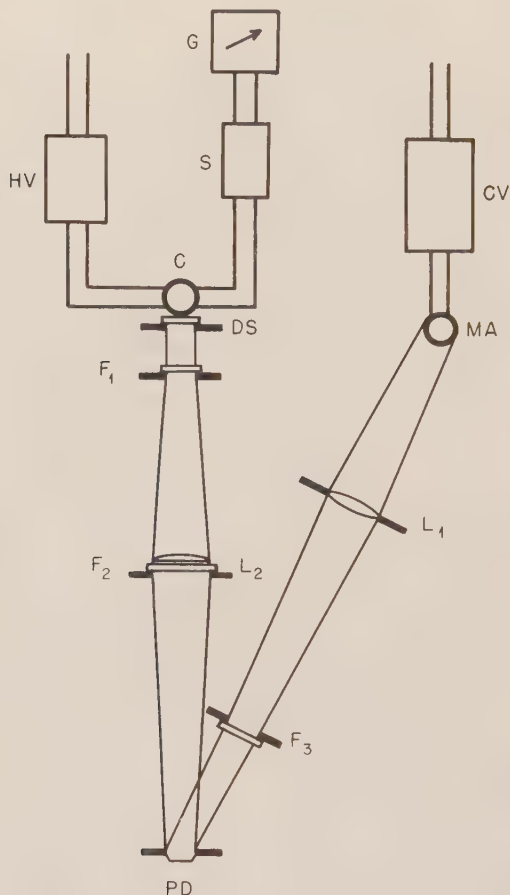


Fig. 24.19—Schematic diagram of high-sensitivity fluorometer. G, galvanometer; S, shunt; HV, high-voltage power supply; C, photocell RCA-IP-21; DS, diffusion-screen aperture; MA, mercury arc A-H4; F₁, filter No. 9780; F₂, filter No. 3484; F₃, filter No. 5860; L₁ and L₂, lens; PD, platinum dish; CV, Sola constant-voltage ballast.

Price, Ferretti, and Schwartz³³ developed an instrument of which the chief requirement was considered to be high sensitivity. This was achieved by using a very sensitive detector and by minimizing the background due to scattered light and fluorescence of the instrument

itself. Several models were developed in the course of their work, and a sensitivity equivalent to less than 1×10^{-11} g of uranium was finally attained. However, residual fluorescence in the sodium fluoride used limited the range to amounts greater than about 5×10^{-10} g. Figure 14.19 is a schematic diagram of one of their instruments. The filter combination isolates the 365 m μ lines and permits detection of the yellow-green fluorescence. It was found that the No. 3484 filter, which absorbs the ultraviolet, is fluorescent and must be chosen from a batch in which this phenomenon is a minimum. Furthermore,

Table 24.1—Response of Fluorometer to Various Materials*

Material	Galvanometer response
1 γ of U in NaF	336,000
Black velvet	74
NaF blank (best obtained)	44
Clean platinum crucible cover	0.5
Platinum crucible cover filled with powdered graphite	0.0

* See reference 33.

the filter must be mounted in the instrument at a point where its fluorescence from the ultraviolet light scattered by the sample will be a minimum. The scattered light was reduced by the use of apertures and black velvet lining. As an indication of the extremely low background attained as a result of these measures, the results obtained by placing the materials listed in the position of the platinum dish are presented in Table 24.1.

The RCA-IP21 photocell that is used, although similar to the No. 931 photocell, is somewhat more sensitive and stable. The circuit is given in Fig. 24.20. The multiplier photocell is more sensitive by many orders of magnitude than the barrier-layer cell or photoelectric cell plus amplifier used in commercial fluorometers in that it provides amplification up to 10^6 . Furthermore, the response is linear over a range of more than 10^6 . For use at maximum sensitivity, the tube must be cooled with dry ice.

For the fluorometric determination of uranium in a phosphoric acid or sulfuric acid medium, the apparatus as shown in Fig. 24.21 has been useful.⁴⁵ The sample in a 1-ml volumetric flask is heated in an aluminum block with phosphoric or sulfuric acid and cooled in a dry ice-methanol bath. The sample is then held at the focal point of the light source and viewed with a hand spectroscope. The uranium concentration is determined by comparison with standards.

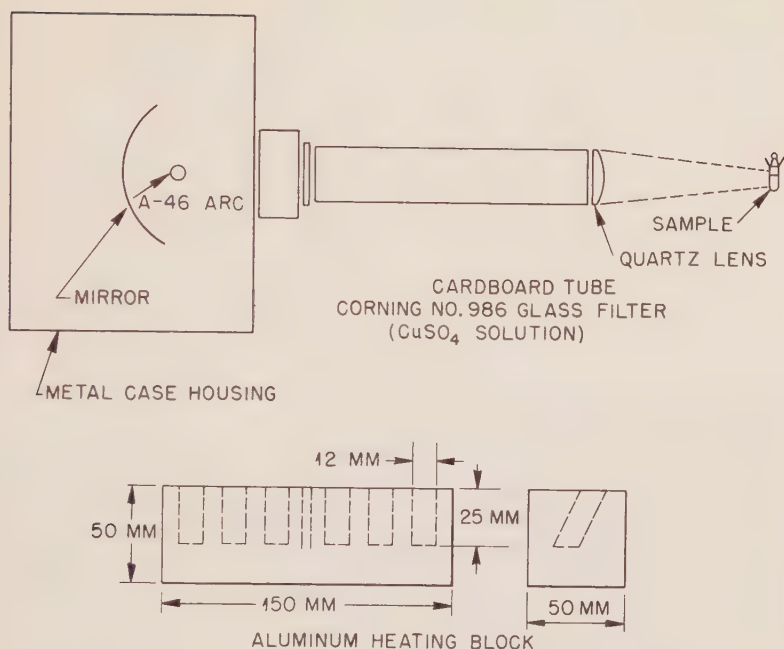


Fig. 24.21 — Fluorometric apparatus for the estimation of uranium.

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Chapter 25

ELECTROMETRIC METHODS

By N. H. Furman and J. I. Watters

Advances in the field of electronics during the past few years have resulted in the transfer of chemical electrometric methods from the research category to one of broad general utility in many lines of work, including control operations. Electronic amplifier circuits for measuring both potential differences and currents, the visual tuning indicator ("magic eye"), the electronic oscillator, and recording galvanometers are incorporated into a variety of analytical apparatus.

Practically all the recent types of instruments used in analytical chemistry are presented in a review of instrumental methods by Mueller.¹ The theoretical principles of electrometric methods are treated in a text by Kolthoff and Laitinen² and in monographs by Sand³ and by MacInnes.⁴ Instrumental principles are discussed in the treatise by Reilly and Rae.⁵

Uranium and other elements of the actinide series are readily titrated potentiometrically, and their state of aggregation is greatly influenced by pH. Consequently, the portable pH meter was considered a necessity in practically every chemistry laboratory both for pH testing and potentiometric titrations. Conductometric titration methods were found to be not particularly well adapted to these elements, but conductivity measurements were frequently employed, especially for the testing of water. The polarograph was employed in various cases.

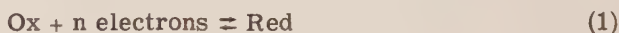
In agreement with most analytical texts and all polarographic data, potentials as recorded in this volume will follow the European convention in which the potential sign corresponds to the actual charge on the electrode. Tables of potentials following this convention are readily recognized since the standard potential for a couple of which the oxidized form is a strong oxidizing agent, such as MnO_4^- or Ce^{+4} , has a positive sign, whereas active metals have a negative sign.

The theoretical discussion of potentiometric methods, polarography, and conductivity measurements will be confined to brief surveys since good monographs on these subjects, to which reference will be made, are available.

1. POTENTIOMETRIC METHODS

1.1 Theoretical Considerations. The general principles and techniques of potentiometric methods are well documented. Potentiometric titrations are extensively discussed in monographs by Mueller,⁶ Kolthoff and Furman,⁷ and Boettger.⁸ A recent detailed review with bibliography has been made by Furman.⁹ Latimer's¹⁰ monograph briefly discusses the theoretical aspects of potentials and critically evaluates available data for the various elements.

It is readily shown on the basis of thermodynamic considerations that for an electrode reaction such as



the potential of the electrode containing finite concentrations of both the oxidized and reduced forms is expressed in terms of activities by Eq. 2.

$$\pi = \pi_0 + 0.059 \log \frac{a_{\text{Ox}}}{a_{\text{Red}}} \quad (2)$$

where π is the potential with reference to the normal hydrogen electrode (N.H.E.), π_0 is the standard potential, and a_{Ox} and a_{Red} are the activities of the oxidized and reduced forms, respectively. If hydrogen or hydroxyl ions enter the electrode reaction, their activities raised to the proper powers appear in the logarithmic expression. When all species involved are at unit activity, the potential of the electrode with reference to the normal hydrogen electrode becomes equal to the standard potential.

It is evident that ions in the solution that form complexes with either or both of the redox forms will alter the potential. In the absence of other complex-forming species the two forms are usually complexed with the solvent. In aqueous solution they are hydrated. Standard potentials for simple hydrated couples are accordingly best measured in solutions of perchlorates or sometimes nitrates. Even these ions may form complexes. However, analytical procedures are nearly always performed in complex-forming mediums. Consequently, a suitably altered equation including the standard potentials for the particular complex ions involved must be used.

(a) Formal Potentials. In practical analytical work it is expedient to substitute concentrations for activities. Equation 2 can be written as

$$\pi = \pi_0 + \frac{0.06}{n} \log \frac{f_1}{f_2} + \frac{0.06}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} = \pi_f + \frac{0.06}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \quad (3)$$

where f_1 and f_2 are activity coefficients of oxidant and reductant. The formal potential π_f is more easily obtained from analytical data than the standard potential since the calculation of activity coefficients is not necessary. Furthermore, the formal potential remains practically constant at a constant ionic strength, such as is obtained in a given procedure, and thus has a practical significance in analytical work.

Since the reactions during most titrations are not truly reversible, the above equations will not be strictly reliable. Thermodynamic reversibility of the reaction, although desirable, is not necessary. It is only necessary that $\Delta\pi$ per Δml of titrant reach a maximum at the equivalence point.

(b) Reference Electrodes. The hydrogen reference electrode, which is inconvenient to use, is generally replaced by a saturated calomel electrode, which is readily prepared and retains a constant potential 0.246 volt more positive than that of the standard hydrogen electrode. Potentials given in reference to the saturated calomel electrode are indicated by the letters S.C.E. However, the normal calomel electrode, N.C.E., which has a potential of +0.282 volt (referred to N.H.E.), frequently serves as the reference electrode in European electrometric data. If a reference electrode with a more positive potential is desired or if chlorides are objectionable, the saturated mercurous sulfate electrode, S.S.E., which has a potential of +0.65 volt (referred to N.H.E.), is extremely convenient. When no reference electrode is specified, the normal hydrogen electrode is implied, but many authors have neglected to mention the reference electrode even though special reference electrodes were used.

(c) Indicator Electrodes. Indicator electrodes may be sensitive primarily to certain specific ions, or their potential may depend on any of several ions. The indicator electrodes discussed below have been used.

Noble-metal electrodes of platinum or gold, which are not specific, may be used to measure the oxidation potential of the solution containing various redox couples such as $\text{Pu}^{+4}/\text{Pu}^{+3}$ or $\text{UO}_2^{++}/\text{U}^{+4}$. In general, when two or more redox couples are present in a solution but are not in true equilibrium, the potential of a noble-metal electrode is determined primarily by that couple having the greater elec-

trode reaction rate. This in turn depends not only on the relative magnitude of reaction velocity constants but also on the concentrations. For example, oxygen dissolved from the air is a fairly strong oxidizing agent in acidic solutions. Because the oxygen electrode reaction rate is slow, the presence of oxygen does not influence the potential measurements of the ferrous-ferric couple at total iron concentrations of the order of 0.1M. However, the dissolved oxygen has a marked effect on the potential if the total iron concentration is reduced to about 0.001M as is necessary in studying rare elements. It is frequently advisable to remove dissolved oxygen from very dilute solutions prior to the titration by bubbling some inert gas through the solution for several minutes. In addition to its effect on the potential, there may be appreciable oxidation by oxygen. Potential-determining impurities may limit the dilution at which a titration will succeed. Any of several noble-metal electrodes, such as platinum or gold, are useful in titrations with oxidizing or reducing agents.

In strongly reducing solutions the hydrogen that is often liberated causes the electrode to behave as a hydrogen electrode. Accordingly, because the overvoltage of hydrogen on mercury is very high, various chemists have employed mercury as an indicator electrode in potentiometric studies of systems such as $\text{Cr}^{+3}/\text{Cr}^{+2}$, $\text{Ti}^{+3}/\text{Ti}^{+2}$, $\text{V}^{+3}/\text{V}^{+2}$ (see reference 11), and $\text{U}^{+4}/\text{U}^{+3}$ (see reference 12).

Tungsten wire, which normally has a thin oxide coating, is more sensitive to pH than to redox couples. For this reason a tungsten-wire electrode is often used in commercial instruments as a reference electrode for redox titrations in which there is no great change in the pH at the equivalence point. Certain other metals such as antimony behave in a similar manner. Other electrodes at which the electrode reaction is very sluggish may also be used as reference electrodes. These electrodes are used chiefly as the insensitive or reference electrode in the so-called "bimetallic" electrode systems for titrations with reducing or oxidizing agents.

Some pH measurements have been made by means of the glass electrode, using a saturated calomel reference electrode.^{15,16} Sensitive vacuum-tube potentiometers permit the use of fairly thick, durable glass electrodes.^{15,16} That a soft-glass surface assumes a potential which is a function of the concentration of hydrogen, sodium, and other ions is well known. Glass of the proper composition is sensitive to hydrogen ions with only a small effect due to large variations in sodium-ion concentration. The potential varies linearly with the pH over a wide pH range of 1 to about 10. Measurements with the glass electrode should always be made with reference to known buffers of pH and composition similar to the unknown. With this precaution the glass electrode is the most reliable and practical means for deter-

mining the pH of solutions containing oxidizing or reducing agents. Of the metals commonly present in solution, sodium produces the most serious effect. Most commercial electrodes have calibration curves for correcting the "sodium error." The electrode is very useful for neutralization titrations of weak acids or bases.

(d) Titration Curves. Since titration curves prepared by plotting potentials vs. volume of reagent added are comprehensively treated in standard analytical texts, their significance will be only indicated here. Before the end point is reached, the potential is determined by the concentrations of oxidized and reduced forms of the substance being titrated since finite concentrations of both its forms are present. When the titration is 50 per cent complete, the concentrations of its oxidized and reduced forms are equal. It can readily be observed from Eq. 3 that at this point the formal potential of the substance titrated actually is measured or can easily be calculated. The formal potential should not differ greatly from the standard potential obtained in the literature¹⁰ for the same couple in a similar solution.

The potential at the equivalence point is theoretically described by the following equation, which usually holds if the hydrogen-ion concentration is unity or if no hydrolysis is involved:

$$\text{End point} = \frac{b\pi_{f'} + a\pi_{f''}}{a + b} \quad (4)$$

$\pi_{f'}$ and $\pi_{f''}$ are formal potentials for the titrated substance and the titrant, and a and b are the numbers of electrons gained or lost by each.

Past the end point the potential is determined by the titrant. The formal potential is readily calculated by the substitution of analytical data into Eq. 3. For example, at 10 per cent past the end point the ratio $[\text{Ox}]/[\text{Red}]$ for the titrant is either 10/1 or 1/10 depending on whether the titrant is a reducing or an oxidizing agent.

1.2 Potentiometric Apparatus. (a) Potentiometers. Most potentiometric titrations can be performed with an ordinary student-type potentiometer. However, almost every laboratory has a compact commercial vacuum-tube potentiometer in the form of a pH meter, which is an ideal instrument for occasional potentiometric titrations. Any of the indicator electrodes already discussed can be used. Millivolts can be read directly if the instrument has a switch for this purpose, or a conversion table can be used for converting pH readings to potentials.

(b) Preparation of Electrodes and Bridges. Extension electrodes can readily be connected to the instrument, preferably by means of a reversing switch. The electrodes, with the exception of the glass

electrode, can be constructed in a short time in the laboratory or can be purchased complete.

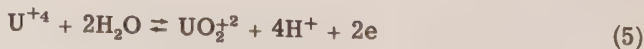
The saturated calomel electrode is prepared by shaking a little dry mercury, calomel, and potassium chloride until the mercury is dispersed and then shaking the mixture with enough saturated solution of potassium chloride to fill the cell. Three per cent agar for salt bridges is prepared by adding 3 g of shredded agar to 100 ml of cold water and gently boiling with constant stirring until the shreds disintegrate. The appropriate amount of potassium chloride or potassium sulfate is then added to produce the desired salt concentration.

Liquid-filled salt bridges with sintered-glass or ground-glass caps at the ends are often convenient. Electrolytic contact can also be made by sealing an asbestos fiber into the end of the glass tube. Platinum electrodes are prepared by sealing platinum wire approximately 0.4 mm in diameter through the end of a soft-glass tube with about 1 cm extending beyond the glass. The electrode must be carefully annealed. Pyrex tubing can be used if the part of the platinum forming the seal is flattened to about one-half its diameter.

1.3 Potentiometric Titrations. (a) Oxidation-Reduction Potentials of Uranium. Uranium exhibits stable valence states of +4 and +6 in solution. Uranium(III), which forms a purple complex in hydrochloric acid and a reddish-brown complex in sulfuric acid, can be obtained but is oxidized slowly by hydrogen ion and rapidly by oxygen of the air to uranium(IV), which has a rich green color. If a salt of uranium(V) is dissolved in water, the uranium disproportionates into states +4 and +6. However, recent work strongly indicates that a small amount of uranium(V) remains in equilibrium with the other two states. According to Heal¹² the equilibrium concentration of uranium(V) is increased by light.

In most potentiometric titrations uranium is oxidized from uranium(IV) to uranium(VI), or uranium(VI) is reduced to uranium(IV). However, zinc amalgam, the most generally used reducing agent, reduces uranium(VI) to a mixture of uranium(IV) and uranium(III). The solution may then be air-oxidized to the uranium(IV) state and titrated with an oxidant. It may also be titrated directly on the basis of potential jumps that occur upon quantitative oxidation to uranium(IV) and uranium(VI), respectively. Accordingly, both the $\text{UO}_2^{+2}/\text{U}^{+4}$ and the $\text{U}^{+4}/\text{U}^{+3}$ couples are important in analytical chemistry.

Uranyl-Uranous Couple. It has repeatedly been observed that the behavior of this couple at a noble-metal electrode can be described at least approximately by the equation



Khlopin and Gurevich¹⁷ recently obtained +0.407 volt (N.H.E.) for the standard potential, which is in good agreement with older data. This value is reasonable on the basis of entropy calculations by Latimer.¹⁰ However, Heal¹² has pointed out that the electrode behavior is not truly reversible since oxidation of uranium(IV) does not occur when the potential of the electrode is increased above its equilibrium value.

Taylor and Smith^{13,14} found that the values for E_0 (N.H.E.) ranged from 0.3202 to 0.3387 volt in solutions that ranged from 0.2000 to 2.000 molal in hydrochloric acid. Polarographic data cannot be used to substantiate this value since a different electrode reaction is obtained in which the uranium(VI) is reduced to an unstable uranium(V) at the dropping-mercury electrode. Thus



The unstable intermediate disproportionates immediately into uranium(IV) and uranium(VI) if the pH is close to zero. Accordingly, on the basis of the polarographic behavior the normal potential for the reaction in Eq. 5 must be more positive than +0.063 volt (N.H.E.), which is the half-wave potential at the dropping-mercury electrode for reaction 6.

Uranium (IV)/(III) Couple. Khlopin and Gurevich,¹⁷ in recent attempts to measure the potential of the uranium (IV)/(III) couple using a platinum electrode, observed that the potential was close to that of the hydrogen electrode. It was indicated by Heal that they were probably measuring the potential of a hydrogen electrode. This follows from the fact that uranium(III) can reduce the hydrogen of water. On this basis Latimer¹⁰ estimates the standard potential of the couple to be approximately -0.5 volt (N.H.E.).

The half-wave potential obtained by Harris^{18,19} for the step-by-step reduction of uranium(IV) to uranium(III) at the dropping-mercury electrode in 1M perchloric acid is -0.68 volt (N.H.E.). Since the electrode reaction is reversible according to Heal¹² and nearly so according to Harris,^{18,19} the standard potential must be approximately -0.68 volt (N.H.E.).

It should be feasible to titrate strong reducing agents such as uranium(III) by using a mercury electrode on which the hydrogen overvoltage is sufficiently high to eliminate the hydrogen electrode behavior.

Bricker, Furman, and McDuffie²⁰ have observed, using a mercury-pool cathode to separate certain metallic ions, that the presence of uranium at 0.8M to 1.0M concentration keeps the potential of the cath-

ode sufficiently low to prevent the electrolytic separation of chromium, manganese, and molybdenum. This is due to the depolarization of the electrode at a potential corresponding to the partial reduction of uranium(IV) to uranium(III). The uranium(III) is reoxidized by hydrogen ion or by oxygen dissolved in the solution from the air or liberated at the anode, and the cycle is repeated. The cathode-potential buffering capacity of uranium has been used by these authors to separate chromium, manganese, and molybdenum from cadmium, cobalt, copper, iron, lead, nickel, and zinc, which are completely deposited at lower cathodic potentials.

(b) Potentiometric Titration of Uranium. The early literature with references complete to 1936 is cited in "Gmelins Handbuch,"²¹ and the various titrations and the interferences are discussed in "Volumetric Analysis,"²² and "Potentiometric Titrations,"²⁷ by Kolthoff and Furman. Furman and Schoonover²³ also reviewed the earlier literature.

In general, uranium(IV) may be titrated to uranium(VI) with any good oxidant such as potassium permanganate,²⁴ ceric salts,²³ potassium bichromate,²⁵ potassium bromate (with ferric and cupric salts added as catalysts),²⁶ or even ferric iron.²⁷ It is not practical to reduce uranium completely to uranium(III). A mixture of uranium(IV) and uranium(III) may be titrated with any of the oxidants mentioned; the amount of reagent used between the two end points is equivalent to the uranium. In general a solution containing 2 ml of sulfuric acid per 100 ml is reduced in the Jones reductor. If the uranium(III) is aerated, an excellent potentiometric indication of the end of the conversion to uranium(IV) is obtained. The air is displaced by an inert gas, and the solution is heated to 80°C and titrated with a standard solution of potassium permanganate or ceric sulfate. If ferric sulfate or chloride is added as a catalyst and if the acid concentration is increased to 4N, the uranium(IV) may be titrated at room temperature with potassium permanganate, potassium bichromate, or ceric sulfate. The titration may also be made with 0.1N ferric sulfate in a solution of sulfuric acid (50 ml of sulfuric acid plus 950 ml of water); 10 ml of 0.1M chromic sulfate is added before the titration, and the solution is heated to 90 to 95°C during titration.²⁸

Uranyl solutions may be titrated with titanous chloride solution at 55 to 60°C in an inert atmosphere. The addition of a considerable amount of Rochelle salt is advisable.²⁹

Interferences. Determination in Mixtures. Nickel interferes seriously with the reduction of uranium in a Jones reductor and less seriously if liquid zinc amalgam is used.³⁰ In general, it is desirable to remove metals of the hydrogen sulfide group and iron, vanadium,

molybdenum, and titanium. Except in simple cases one or more of the following processes will need to be applied: cupferron extraction (to remove iron, titanium, vanadium, molybdenum, etc.), hydrogen sulfide precipitation, mercury-cathode electrolysis, and ether extraction. Nitrates should not be present during the reduction and titration. Acetates are not harmful.²³ There is a considerable latitude in the concentration of sulfuric acid that must be present during the titration, from 2 to 20 to 30 per cent by volume having been used.

Any two or all three of the elements uranium, vanadium, and iron may be determined by a succession of abrupt potential changes during the titration of the solution after reduction.³¹⁻³⁴ If all three elements are present, the solution is titrated first at 80°C in an inert atmosphere to a first end point, A, corresponding to oxidation of vanadium(II) to vanadium(III) and uranium(III) to uranium(IV). Between this first point, and the second, B, vanadium(III) and uranium(IV) are oxidized simultaneously to vanadium(IV) and uranium(VI). The solution is then cooled to room temperature, and the ferrous iron is titrated to ferric as marked by a third end point, C. Finally the solution is heated to 80°C, and vanadium(IV) is titrated to vanadium(V) with a fourth end point, D. The uranium is found by subtracting the amount of reagent between points C and D from that between points A and B.

The behavior of titanium has been studied by Someya,^{35,36} Treadwell and Blumenthal,³⁷ Kikuchi,³⁸ and Khlopin and Kaufman.³⁹

Various Prereduction Methods. Luyckx⁴⁰ and Gantz et al.⁴¹ used the mercury cathode to reduce uranium. The metals zinc, cadmium, lead, bismuth, copper, and silver have been commonly employed. Birnbaum and Edmonds⁴² first proved that silver in 4M hydrochloric acid solution at 60 to 90°C reduces uranium(VI) only to the uranium(IV) state. This process was used extensively on the Project. Nakazono⁴³ found that liquid zinc amalgam (1 to 2 per cent zinc) reduced uranium quantitatively to the quadrivalent state. Furman, Mason, and Pekola⁴⁴ have used the latter process repeatedly for the determination of macro amounts of uranium. The noninterference of nickel during reduction with either silver or liquid zinc amalgam is noteworthy.

Titration Curves. On the basis of typical graphs by Ewing and Eldridge,²⁴ in which 0.7N sulfuric acid was used, it is observed that the potential remains at about -0.32 volt (N.H.E.) until the uranium(III) is oxidized. This is higher than the standard potential for the uranium (IV)/(III) couple and is due to the effect of liberated hydrogen on the platinum electrode potential. The H^+/H_2 and the uranium (IV)/(III) couples, which obviously are not in full thermodynamic equilibrium throughout the solution, establish an intermediate potential at the sur-

face of the platinum electrode, which behaves as a surface catalyst. The result is a potential between that produced by the two electrodes separately.

If an electrode of a metal such as mercury, which has a sufficiently high hydrogen overvoltage, had been used, the potential at the first end point could have been expressed as

$$\text{End point} = \frac{2f[\text{U(VI)}/\text{U(IV)}] + 0.24 \log [\text{H}^+] + f[\text{U(IV)}/\text{U(III)}]}{3} \quad (7)$$

Using this equation the theoretical end point is calculated to be -0.03 volt (N.H.E.), which compares well with the observed end point of about 0.0 volt (N.H.E.). According to Luyckx⁴⁰ the first end point for the titration of uranium(III) is accurate if the titration is performed at a temperature of about 80°C . At room temperature the potential break occurs too late, presumably owing to the slow oxidation of the hydrogen layer by the titrant.¹²

The mid-point of the second plateau has a potential of $+0.42$ volt (N.H.E.), which is in good agreement with the standard potential of the $\text{UO}_2^{+2}/\text{U}^{+4}$ couple.

The second end point for the completion of the titration of uranium(IV) to uranium(VI) evidently occurs at the equivalence point independently of the concentration of the acid or the temperatures. This potential depends on the titrant used as indicated in Eq. 4 and is usually of the predicted magnitude.

Titration of Uranyl Salts with Alkali. MacInnes and Longworth⁴⁴ determined the pH values at 20 to 25°C of several uranyl salt solutions of various concentrations. A portion of their data is presented in Table 25.1.

A fairly sharp break in the graph of pH vs. moles of HCl per mole of UO_3 was found at 2 moles of acid per mole of oxide. The pH at this point was 1.92 at $(\text{Cl}^-) = 1$, 2.25 at $(\text{Cl}^-) = 0.5$, and 2.76 at $(\text{Cl}^-) = 0.1$.

Titration of Mixtures of Uranium(VI) and Uranium(IV) with Alkali. Harned⁴⁹ and associates attempted to precipitate uranoso-uranyl hydroxide by potentiometric titration of a mixture of uranous and uranyl sulfates, in proper proportions, with sodium hydroxide. It was observed that the first precipitate to form appeared to be uranous hydroxide, after which a uranyl compound was precipitated. There was no noticeable change in pH between the formation of the uranous and the uranyl precipitates.

(c) Determination of Acid in the Presence of Uranium. In general it has been found possible to determine free acids potentiometrically in the presence of uranyl salts. The earlier work of Britton⁴⁵ has

been reviewed and extended by Harris^{18,19} and Kunin.⁴⁶ It is found that the number of equivalents of alkali added between the first break in pH and the second is dependent upon the dilution, the temperature, and the rate of addition of the alkali. Kunin⁴⁶ found the second break at an average ratio of 2.22 moles of alkali per mole of uranium when mixtures of hydrofluoric acid and uranyl fluoride were titrated.

Van Name et al.⁴⁷ and Hammond et al.⁴⁸ found a method for determining free nitric acid in a solution containing uranyl, ferric, aluminum, nickel, copper, calcium, barium, and sodium nitrates. The

Table 25.1—pH of Solutions of Various Uranyl Salts

Conc. of uranyl salt, equiv. per liter	pH measured			
	UO ₂ Cl ₂	UO ₂ (NO ₃) ₂	UO ₂ SO ₄	UO ₂ (C ₂ H ₃ O ₂) ₂
0.001	4.05	4.05	4.17	4.76
0.01	3.41	3.41	3.595	4.55
0.1	2.76	2.78	2.915	4.24
1.0	1.92	1.91	1.97	

uranium and other ions that form slightly soluble ferrocyanides are precipitated by adding potassium ferrocyanide and saturating the solution with potassium nitrate. After diluting to a definite volume with saturated potassium nitrate, the precipitate is centrifuged, and the volume is noted. The clear solution is titrated, and the graph in the region of pH 3.5 to 4 is carefully plotted. By superimposing a curve for normal nitric acid titrated with the same alkali it is possible to extrapolate to pH 7. Direct titration to this point is not possible because of the presence of aluminum, which begins to use alkali beyond pH 4. This procedure is given in detail in Chap. 3, "Nitrogen."

(d) Other Titrations. Atanasiu⁵⁰ titrated uranium(VI) in acetate solution containing 35 per cent alcohol with potassium ferrocyanide at 70°C, but there were many interferences.

Many well-established potentiometric titration methods, e.g., halide determinations,⁵¹ were utilized.

One interesting application of the concentration-cell principle in the ultramicro range was made by Koch and Wilmarth⁵² for the ultramicrodetermination of fluoride. The principle of measuring the effect of fluoride ion on the ferric-ferrous electrode that had previously been used by Low and Pryde⁵³ to determine fluoride was extended to the ultramicro range. The cell consisted of a drop of ferric-ferrous solution suspended between a small gold-foil electrode and a capillary

that was filled with agar and KCl and led to a calomel electrode. The drop was kept in an atmosphere saturated with water vapor. A resistance was inserted in the circuit to the amplifier and potentiometer in order to prevent electrochemical changes in the cell due to drain of current or the reverse while balancing the potentiometer. One-tenth microgram of fluoride produced a potential of approximately -35 mv. Although the absolute emf of the cell was not reproducible, the changes in emf per 0.1 γ of fluoride, per 0.2 γ of fluoride, etc., could be duplicated to ± 0.2 mv.

2. POLAROGRAPHIC METHODS

These methods, which were first developed by Heyrovsky and his associates, are well described as to theory, instruments, and techniques in monographs by Heyrovsky,⁵⁴ Kolthoff and Lingane,⁵⁵ Mueller,⁵⁶ and Hohn.⁵⁷ Bibliographies arranged by subjects, authors, and years have been published by the E. H. Sargent & Co.^{58,59} and the Leeds & Northrup Co.⁶⁰

In brief, the registering or the observation of a current-voltage curve as an increasing emf is slowly and continuously applied to a polarizable electrode relative to a reference electrode is the fundamental principle of the method. The polarized electrode is usually one of mercury dropping from a capillary. For certain purposes a rotating platinum microelectrode may be used. The reference electrode is commonly a saturated calomel electrode joined to the system by an agar bridge. A rather large mercury electrode (1 to 3 cm in diameter) frequently serves. The small electrode may be anodically polarized to points short of the anodic solution of mercury, or cathodically to the point where the supporting electrolyte, which is frequently a buffer mixture, gives a large increase in current or a "terminal wave." The supporting electrolyte is in general at least 25 times as concentrated as the substance to be determined.

Given an adequate supporting electrolyte that is many times as concentrated as the substance to be reduced, it is well known that reduction of ions or of molecules is indicated by a "wave," i.e., an increase in current to a limiting value. The height of the wave is a measure of the quantity of the reducible substance.

The potential at which the wave attains half its height after correction for the residual current of the supporting medium is characteristic for the reducible ion. It is designated as the "half-wave potential." True half-wave potentials also involve a correction for the voltage drop due to the resistance of the cell.

The limiting current with an excess of supporting electrolyte present is dependent upon thermal diffusion and is called a "diffusion cur-

rent, i_d ." Ilkovič⁶¹ derived Eq. 8 for the average diffusion current by a consideration of the fundamental laws of diffusion and those of electrochemistry.

$$i_d = 605nCD^{1/2}m^{2/3}t^{1/6}\mu a \quad (8)$$

In this equation the concentration C is expressed in millimoles per liter; D , the ionic diffusion constant, is expressed in square centimeters per second; m , the mass of mercury flowing is expressed in milligrams per second; and t , the drop time, is expressed in seconds. The geometric constants and the faraday in the proper units give the constant 605. Several of the terms that enter into the equation are temperature-dependent. If a room of fairly constant temperature is

Table 25.2—Relative Values of Capillary Characteristics at Various Potentials vs. S.C.E.

Potential, volts	Relative value
0	0.985
0.2	0.99
0.3 to 0.8	1.00
0.9	0.99
1.1	0.98
1.3	0.97
1.5	0.95
1.7	0.93
1.9	0.91

available, thermostating is unnecessary provided frequent calibrations are made. For precise work the use of a thermostat is necessary since the diffusion current increases approximately 2.5 per cent per degree of temperature rise.

Many analytical problems can be handled by empirical calibrations that establish the range over which i_d is proportional to C . For every capillary the characteristic $m^{2/3}t^{1/6}$ should be determined. With the aid of this constant it is possible to compare the observations of various investigators or to make use of data obtained with a capillary of different characteristics.

For a given capillary with a mercury head of more than 20 cm the mass of mercury delivered per second is practically independent of the potential, but the drop time changes rapidly. As a result the capillary characteristic and consequently the diffusion current changes with the applied voltage. The capillary characteristic can be meas-

ured at -0.5 volt vs. S.C.E. and calculated for other voltages by multiplying by its relative value (see Table 25.2). Therefore, in accurate work in which the height of a second wave is to be determined, a correction should be applied to the first true diffusion current measured at the first potential before subtracting it from the total diffusion current at the second potential. Details are discussed by Kolthoff and Orlemann.⁶² The polarographic sensitivity, I , of any ion is defined as the true diffusion current per millimolar concentration of the ion at 25°C divided by the capillary characteristic at the potential of the measurement. Thus

$$i_d = I \times C \times m^{2/3} t^{1/6} \quad (9)$$

Various applications of this equation are at once evident.

Several lines of investigation and analysis were actively pursued. Much new knowledge was gained about the polarography of uranium in various states of oxidation and in various mediums. This material will be presented in detail. The determination of microgram quantities of uranium in dust, filtrates, and many other substances was made very frequently by this method. A new combination of techniques, namely, electrolysis of traces of metals into a mercury cathode to separate them from uranium, followed by distillation of the mercury and polarographic examination of the solution of the residue, was used on samples of uranium, magnesium, dolomite, and other materials. The chief objective was the detection of cadmium. Mercury-cathode separations in nitric acid solutions were applied prior to the estimation of cadmium by the polarographic method.

The dropping-mercury electrode was used to verify the standard potential of the plutonium (IV)/(III) couple, and a highly specific polarographic method was developed for plutonium.⁶³ The trivalent state of neptunium was discovered polarographically using a micropolarographic technique which will be described. On the basis of these waves it was possible to recommend a suitable procedure for obtaining neptunium in the trivalent state.

2.1 Polarographic Apparatus. Polarograms are produced by using instruments that are manually operated or that record automatically. Since the word "polarograph" is copyrighted, diverse names have been applied to the instruments manufactured by various concerns. The automatic instruments are considerably superior when entire current-voltage curves are desired or when the entire curve must be obtained in a short time owing to the changes that occur in the solution. The manual instrument, which can be constructed from readily

available equipment, is satisfactory for measuring diffusion currents at predetermined potentials in the analysis of solutions whose constituents are known. Many solutions can be analyzed quickly and economically using a simple manual instrument such as one to be described.

(a) Automatic Recording Instruments. Two types of automatic recording instruments were used on the Project. The first type developed by Heyrovsky contains a potentiometer drum connected directly

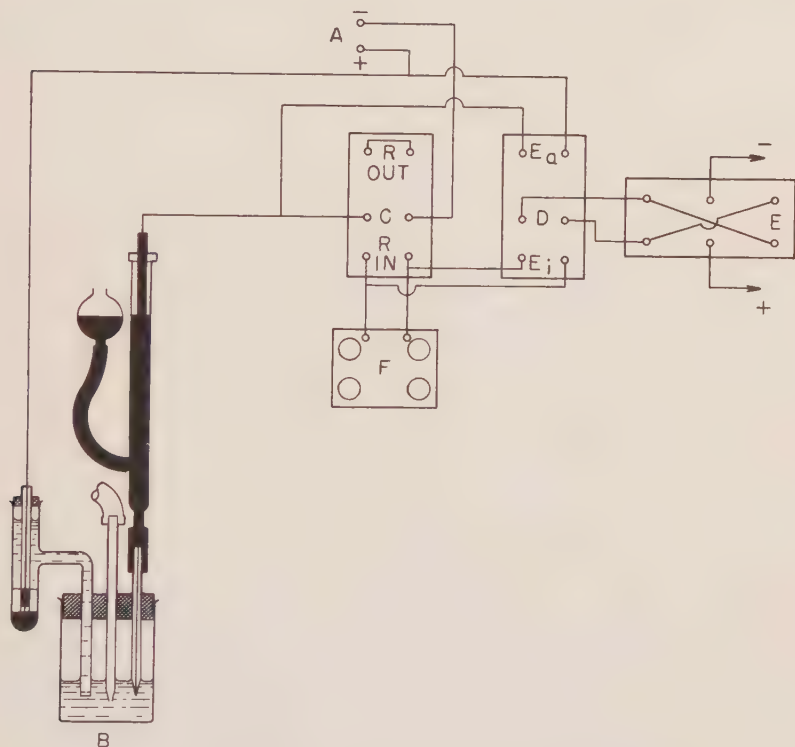


Fig. 25.1—Circuit for current and voltage measurements with potentiometer, connected at E positive and negative.

or through gears with a revolving drum on which is fastened a piece of photographic paper. A light beam reflected from a galvanometer mirror records the current on the paper. In the other type of instrument the potentiometer drum is turned by a synchronous motor. An automatic recording microammeter synchronized with the potential divider records the current by pencil or pen on a graph paper.

(b) Manual Instruments. Even with the automatic instruments, accurate manual potential measurements are frequently desirable. In Fig. 25.1 is shown a schematic diagram of the polarographic-cell assembly and the apparatus used at one site for manually measuring the applied voltage and the current in conjunction with the automatic instrument or without it. Leads A go to the polarograph or its manual equivalent shown in Fig. 25.2. The polarographic cell and electrodes are shown at B in Fig. 25.1. Switches C, D, and E are ordinary porcelain double-pole double-throw knife switches. These switches, although bulky, are used because they are particularly reliable. Switch

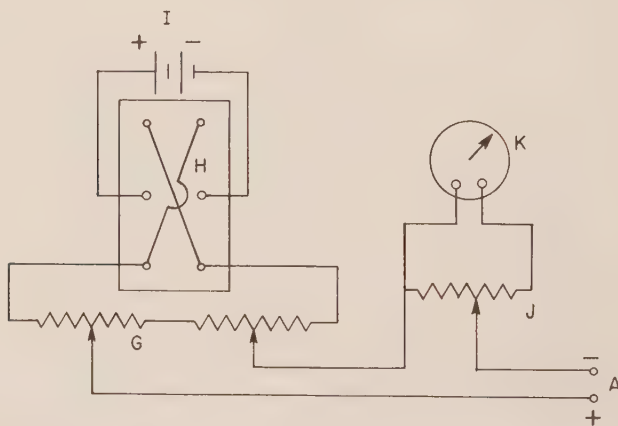


Fig. 25.2 — Manual equivalent of polarograph for use with apparatus in Fig. 25.1.

C permits the inclusion of a 10,000-ohm precision decade resistance box or a precision-fixed 10,000-ohm resistance in the line for determining the current manually by Ohm's law. This resistance should be out during automatic runs. Switch D connects the potentiometer to either the leads at the cell for measuring the applied emf, E_a , or the potential drop, E_i , across the standard resistance. If E_i is observed to be +0.0135 volt across 10,000 ohms, the current is $1.35\mu\text{a}$. For calibrating the galvanometer the polarograph cell can be replaced by any large resistance of 10,000 to 100,000 ohms. The current is measured as above.

E_a consists not only of the potential applied to the cathode vs. the anode but also any IR drop in the region measured, namely, within the cell. For this reason the standard resistance is not included in measuring E_a . The cell resistance is kept as small as possible. To achieve this the agar bridge of the external anode has a relatively large diameter.

Switch E is included if the potentiometer does not contain a reversing switch. The potentiometer circuit is not included since many modern potentiometers are complete in one cabinet. The galvanometer for measuring null points should be of the high-sensitivity spotlight type, and the tapping key should have a provision for placing a fixed resistance of about 75,000 ohms in series with it for measuring large currents. The old student-type potentiometer was excellent because applied voltages as high as 2.3 volts could be measured directly. Newer instruments cannot be used above 1.6 volts without doubling the potentiometer range by adjusting the potentiometer voltage with the standard cell set at one-half its true value.

The apparatus can be used without a polarograph if the manual potential divider shown in Fig. 25.2 is connected to A. G consists of two radio potentiometer-type rheostats having resistances of 60 and 2 ohms for coarse and fine adjustments, respectively. Ohmite rheostats are excellent for this purpose. The potential source I may be two dry cells or two wet cells. The double-pole double-throw switch H permits the application of either positive or negative voltages. The switches must be appropriately labeled. The Ayrton shunt and galvanometer may be included for direct, rapid current reading or may be omitted. The galvanometer of the moving-coil reflecting type should preferably have a period of greater than 6 sec and a sensitivity greater than 0.01μ a per millimeter of scale division at 1 meter.

(c) Electrolysis Cell Assembly. Dropping-mercury Electrode. The main column of the dropping-mercury electrode, Fig. 25.1, is a glass tubing about 80 cm long and 12 mm O.D. with a side arm sealed near the bottom. A leveling bulb is connected to this side arm by means of a long rubber tube. The capillary, a piece of marine barometer tubing (manufactured by Corning Glass Works) of 4 mm O.D., is fastened to the lower end by means of a rather thick-walled piece of rubber tubing. All rubber tubing should be boiled in at least 1N sodium hydroxide and then in water to remove sulfur from the surface. Neoprene tubing, which requires no alkali treatment, can also be used. The capillary should be of sufficient length to produce drops every 1.5 to 4 sec in 0.1N potassium chloride with no potential applied and under a mercury head of 40 to 80 cm. For use in micro cells the tip of the capillary should be tapered to within about 1 mm from the bore on the side of a carborundum glass-cutting wheel. Otherwise, air bubbles which are difficult to dislodge collect on the tip.

Care and Cleaning of Capillary. After use the capillary tip should be rinsed with water, wiped with a Kleenex or with lens paper, and immersed in a deepest tube of mercury. The mercury column should be lowered nearly to the level of the side arm. With clean mercury the capillary should need only infrequent cleaning. Its drop time

should be checked periodically in 0.1N KCl when shorted to a saturated calomel electrode. If a change is observed, dipping the tip in concentrated nitric acid followed by a careful rinsing sometimes corrects the difficulty. If not, the capillary must be removed and cleaned. The tip of the capillary is attached to a water aspirator, and the top is alternately dipped into concentrated nitric acid and then removed and touched against the side wall to remove the excess acid. The passage of air bubbles through the capillary can be observed under an electric lamp placed near the aspirator. The process is repeated with several portions of water. Finally the capillary is dried with a lint-free piece of cloth, and air is drawn through it for several minutes. If this treatment fails, a new capillary should be prepared.

Anode. The insert anode shown in Fig. 25.1 was designed to prevent contamination of solution by prolonged contact with the agar. It should be inserted just prior to the measurements and should be leached out in saturated potassium chloride after using.⁶⁴ A sintered-glass disk can be sealed onto the lower end of the agar bridge, but this is not necessary. The stem is easily filled with 3 per cent agar by first allowing a portion to solidify at the elbow with the cell nearly inverted. The strongest agar is obtained by preparing a 3 per cent agar stock gel and then adding the proper amount of potassium chloride or potassium sulfate to a small portion of the heated agar just before using. The dispersed solid phase is prepared by shaking solid calomel, mercury, and potassium chloride together for a few minutes in a small Erlenmeyer flask.

For obtaining polarograms of waves in the positive region vs. the saturated calomel anode without switching to anodic polarization, it is convenient to use a saturated mercurous sulfate electrode with a potential of -0.4 volt (S.C.E.). This electrode also has the advantage that it can be inserted directly into solutions that must be kept chloride-free.

The anode is designed to have a minimum of resistance. When necessary in micro work the 10-mm O.D. terminal of the outside calomel anode can be replaced by one of 4 mm. This tip can in turn be drawn down to about a 2-mm O.D. tip for direct insertion into the solution in very small micro cells.

Cell. Polarographic cells are generally far more complicated than is necessary. The cell shown in Fig. 25.1 is a tall-form lipless beaker of 25 to 50 ml capacity. Holes are drilled in a rubber stopper to receive the electrodes, the nitrogen bubbling tube, and a trap for the escape of nitrogen. It is convenient to make the holes for the electrodes large enough to receive small one-holed stoppers, which are permanently affixed to the electrodes. Otherwise, care must be ex-

exercised in drilling these holes just large enough to receive the electrodes without force. For many determinations it is best to insert the electrodes just prior to making the measurements and after removing oxygen by bubbling nitrogen through the cell for 15 to 20 min.

Micro Cells. Polarographic studies of many valuable samples must be performed with as little as 100 to 200 microliters of solution.

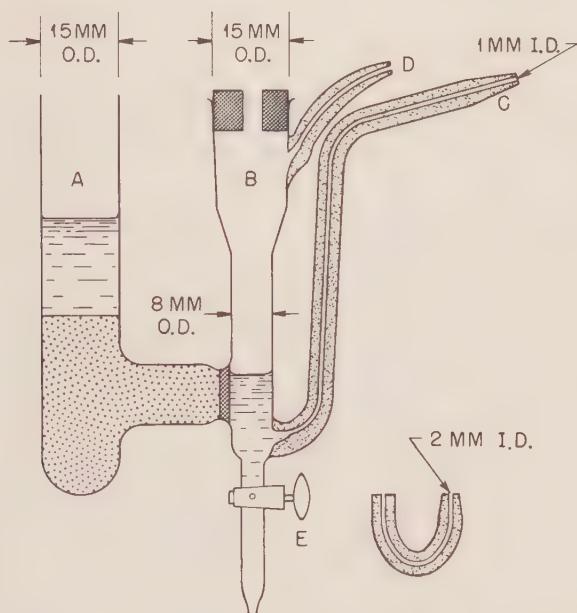


Fig. 25.3—Polarographic cell for 0.3 to 0.5 ml of solution.

Generally the cell must be designed to permit the removal, by a nitrogen stream, of oxygen dissolved from the air, and an arrangement must be made for the removal of mercury in the course of the run since the total mercury-drop volume is large compared to the volume of the solution studied. Furthermore, since chemical reaction with the mercury itself becomes appreciable in either oxidizing or strongly acidic solutions, absence of mercury during the oxygen-removal treatment is often important. The cells and techniques discussed below were developed⁶⁵ for analyzing samples.

The cell shown in Fig. 25.3 has been used for 300 to 500 microliters of solution. The sintered-glass disk, 6 to 8 mm in diameter, is sealed as close to tube B as possible. The glass disk is backed up with 3 per

cent agar containing a suitable electrolyte; this is covered with a layer of the same electrolyte in aqueous solution. The anode shown in Fig. 25.1 is inserted into tube A.

When the cell is in use, nitrogen is passed through the solution by way of tube C for 20 min. The nitrogen is then directed into tube D in order to exclude air while the capillary is being inserted and during

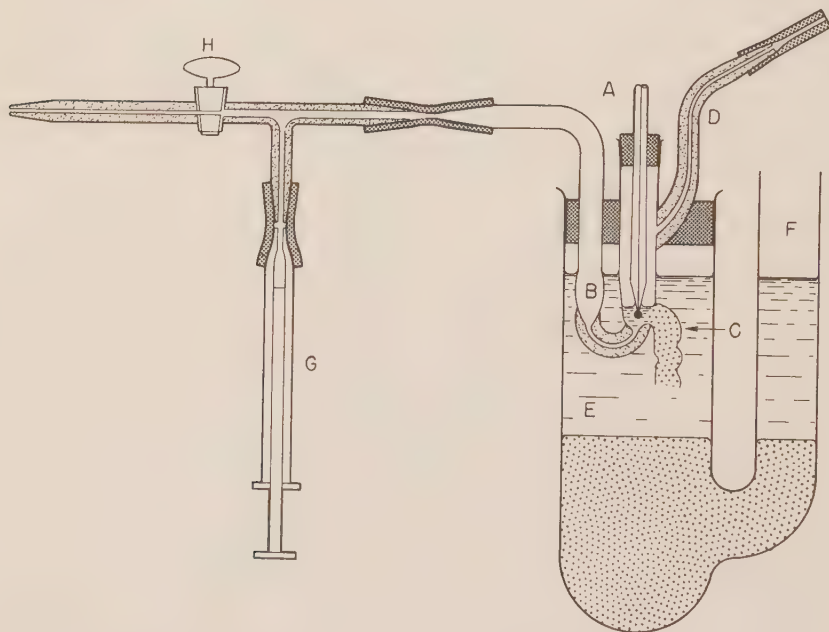


Fig. 25.4—Polarographic cell for 0.1 to 0.2 ml of solution.

the run. The capillary fits loosely into a cork stopper. Mercury is drawn off by stopcock E as required. If it is necessary to lower the mercury during the run, it is best simultaneously to stop the motor and close the camera during this operation. The stopcock can be replaced by the U tube shown in the figure if contact with mercury is not objectionable. The cell must be leached out after each run.

The cell shown in Fig. 25.4 was prepared for use with 100 to 200 microliters of solution although 200 microliters is preferable, especially if the drop mass is fairly large. The cell proper, A, is prepared from a 2-ml pyrex centrifuge cone. The lower portion of the nitrogen bubbling tube B as well as tube D is prepared from 1-mm-bore pyrex capillary tubing. External electrical contact is made

through tube C, which is 5 mm in outside diameter and is filled with 3 per cent agar containing a suitable electrolyte. Indentations prevent motion of the agar.

The entire cell is held in place in a larger tube, E, containing 3 per cent agar under a layer of aqueous solution that has the same electrolyte concentration. The anode shown in Fig. 25.1 is placed in tube F. A tuberculin-syringe control, G, is used to withdraw mercury from the cell.



Fig. 25.5—Simple micro polarographic cell for use when long contact with mercury is not objectionable.

When the cell is in use, nitrogen is first bubbled through the solution by way of tube B by regulating stopcock H until small bubbles rise regularly without spattering. A slow stream of nitrogen is also admitted at tube D to sweep out the cell. The capillary is then inserted just below the surface through a loose-fitting stopper, and stopcock H is closed. Any solution in tube B is easily ejected by means of control G. When it becomes necessary to lower the mercury, both the polarograph camera and motor are stopped while the mercury is carefully pulled into tube B by means of control G. It is best to use a minimum of gelatin or other maximum suppressor that tends to cause the mercury to remain as spheres. The cell is always leached out in the same supporting electrolyte after each determination.

For polarograms in which a mercury-pool anode is not objectionable, the cell shown in Fig. 25.5 has been found very satisfactory. The cell proper is prepared from a 2-ml centrifuge cone. Dissolved oxygen can be removed by means of a nitrogen stream from a fine-tipped capillary tube drawn from 1-mm pyrex capillary tubing. The surface-sweeping tube, D, in Fig. 25.4 may also be added.

2.2 Polarography of Uranium. The polarographic method has found considerable application in the determination of uranium. Its most useful range is 10^{-4} M to 10^{-2} M uranyl ion in strongly acidic solutions. The diffusion current can be measured at -0.3 volt (S.C.E.), and various interfering substances can be eliminated readily. The method can be used for determining the concentration of uranyl ion in the presence of uranium(IV). Uranyl ion in the concentration range of 10^{-5} M to 10^{-8} M can be determined by its catalytic effect on the nitrate reduction wave at -1.2 volts (S.C.E.) in which there are many interferences.

The polarography of uranium, although somewhat involved, is particularly interesting because the electrode behavior furnishes information concerning the chemical behavior of the element. Since hydrogen ions are involved in the electrode reaction, the waves are greatly influenced by the pH of the solution.

Herasymenko^{66,67} first studied the polarography of uranium and, in a qualitative manner, explained the nature of the uranyl waves in dilute solutions of mineral acids. Strub⁶⁸ eliminated the interference of iron(III) by using 2N hydroxylamine hydrochloride as a supporting electrolyte. Harris¹⁸ studied the polarography of uranium(IV) and uranium(VI) in various buffers and quantitatively correlated the wave height of uranyl waves in acidic medium with the pH. Kolthoff and Cohn⁶⁹ studied the uranium wave in acetate solutions. Heal¹² obtained many polarograms of uranium(III), uranium(IV), and uranium(VI) and first observed the anodic uranium(III) wave as well as a cathodic wave for the reduction to the metallic state after the hydrogen wave. Heal studied the Becquerel effect and postulated that the $\text{UO}_2^{+}/\text{U}^{+4}$ electrode potential was determined by a reversible uranium (VI)/(V) couple, whereas the uranium (V)/(IV) couple was irreversible. Tishkoff and Dounce^{70,71} first obtained waves due to the anodic oxidation of uranium(IV) in buffered acetate solutions and correlated the shift of half-wave potentials with possible complexes of uranium and acetates but included no experimental data.

Harris¹⁸ recommended 0.2N hydrochloric acid as the supporting electrolyte for determining uranium. Tishkoff⁷² determined uranium(VI) in uranium(IV) salts using 0.1N hydrochloric acid. Kwiatowski, Owens, and Casto⁷³ determined uranium(VI) in 1.5N sulfuric acid.

Sheel and Watters⁷⁴ found the diffusion current to be nearly constant in 1N to 2N sulfuric acid and discussed the nature of the wave in this medium. Smith⁷⁵ and Ballenger⁷⁶ determined uranium in atmospheric dust after oxidizing organic matter by using 2N sulfuric acid as the supporting electrolyte. Cook and Vroom⁷⁷ determined uranium in the presence of excess thorium in 0.1N to 1N hydrochloric acid after fuming with perchloric acid.

Kilner⁷⁸ used a supporting electrolyte of 2N hydroxylamine hydrochloride and 0.1N hydrochloric acid to determine uranium in a precipitate of ferric hydroxide. Ferric iron was reduced after boiling 2 min, but it was necessary to use electrolysis to remove copper.

Furman and his associates have made extensive use of the polarographic method for determining both uranium and other constituents in ores and other substances. They have employed the mercury-cathode procedure for separating cadmium, cobalt, copper, iron, nickel, lead, and zinc, and other ions from uranium and have developed procedures for determining both the uranium in the aqueous phase and the constituents of the amalgam.⁷⁹⁻⁸³ Haight⁸⁴ found that uranium could be determined in ores without preliminary separation of copper and lead by using a supporting electrolyte that was 1N in hydroxylamine hydrochloride and 5 per cent in sodium tartrate or in 50 per cent diammonium citrate at a pH of 4.0 to 5.5. Morrison and Haight⁸⁵ determined traces of uranium polarographically in solutions containing an excess of copper, iron, nickel, and chromium by using an ether separation. Interferences are considered later in greater detail.

(a) Uranium Waves. Uranyl Waves in Acidic Mediums. The polarogram of uranyl ion in dilute solutions of strong acids consists of a wave with a half-wave potential of -0.18 volt and two coalesced waves with an apparent half-wave potential of -0.93 volt (S.C.E.). Since each wave is due to a one-electron reduction, the polarogram appears to consist of two waves, and the second wave is twice the height of the first, as shown in Fig. 25.6.

Neither the first nor the third half-wave potential is appreciably affected by changes in the acidity or salt concentration. The intermediate $U(V) \rightarrow U(IV)$ wave appears as a distinct wave in more acidic solutions, but in lower acid concentration it is generally coalesced with the $U(IV) \rightarrow U(III)$ wave or masked by an increase in the first wave height resulting from disproportionation, which will be discussed.

Heal¹² has stated that it is possible to obtain a wave corresponding to the reduction of the intermediate uranium(III) to the metallic state in solutions of about 0.01N hydrogen ion. This wave, which follows the hydrogen wave and precedes the potassium wave, has a half-wave

potential of approximately -2.2 volts (S.C.E.) in sulfate solutions and -1.9 volts (S.C.E.) in chloride solutions. It is likely that the standard potential is more positive than -1.9 volts (S.C.E.) because it is stated that uranium probably separates as a finely divided solid on the mercury surface. For comparison, the half-wave potential for the reduction of ferrous iron is -1.2 volts (N.H.E.), whereas the corresponding

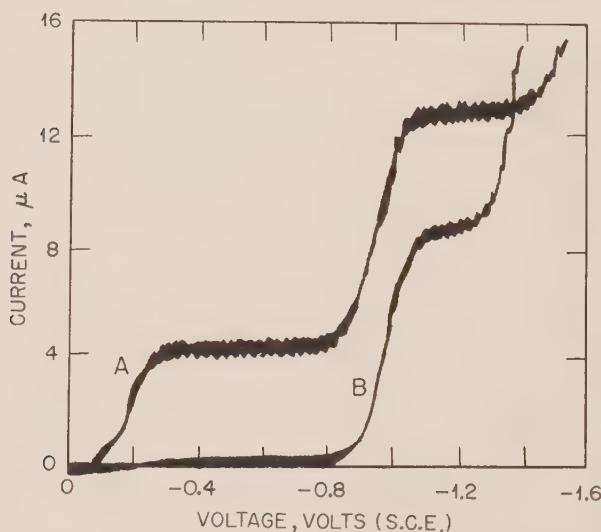
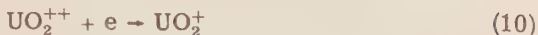


Fig. 25.6—Polarograms of sexivalent and tetravalent uranium.¹⁸ Curve A: Polarogram of 10^{-3}M UO_2Cl_2 , 0.1M KCl , 0.01M HCl . Curve B: Polarogram of $2.08 \times 10^{-3}\text{M}$ UOSO_4 , 0.1M KCl , 0.1M HCl .

standard potential is only -0.44 volt. In the case of cadmium, which is considerably more soluble in mercury, the difference is much smaller. The solubility of uranium in mercury deserves special mention (Report CT-2960). Prior to 1941 all investigators agreed that the solubility of uranium in liquid mercury at 25°C was negligibly small;⁸⁶ values of the order of 0.00001 per cent were ordinarily quoted for it.⁸⁷ Recent work has shown that this result must be attributed to the use of impure or oxide-coated uranium. It was found that pure finely divided uranium metal prepared in an oxide-free state by decomposition of uranium hydride readily amalgamated with mercury to form a silvery pasty mass similar in appearance to other metal-mercury amalgams. Amalgams containing up to 1 per cent uranium are liquid and fairly stable to air. Those containing between 1 and 15 per cent uranium are gray pyrophoric solids.

The first wave is due to reactions such as



Harris¹⁸ found that in hydrochloric acid solutions the first diffusion current increases when the concentration of noncomplexing acids is increased above 0.5N and approaches that due to a two-electron change when the acidity reaches 6N. This increase is due to uranyl ions furnished through disproportionation of the quinquevalent intermediate. This intermediate, formed in the first reduction, undergoes disproportionation at a rate directly proportional to the hydrogen-ion concentration by reactions such as



If the UO_2^{++} formed has not yet diffused away from the drop, it, in turn, is again reduced to the quinquevalent state. At high acidities this alternate reaction consisting of electrolytic oxidation and chemical disproportionation occurs to such an extent that all the uranium ions diffusing to the drop are reduced to uranium(IV) and the diffusion current is doubled.

Harris observed that complexing agents, such as the oxalate ion, which preferentially complex the sexivalent uranyl ion also shift the equilibrium in Eq. 11 to the right and cause an increase in the height of the first wave. For example, in 0.2M oxalic acid the first wave is due to a two-electron reduction. The acidic oxalate supporting electrolyte should be useful for the elimination of the interference of cations forming stable oxalate complexes. Acidic tartrate and citrate solutions^{83,84} have been used for this purpose. In nearly all acidic solutions a second wave with a half-wave potential of -0.9 volt (S.C.E.) increases the total wave height to that corresponding to a three-electron change. Sheel and Watters⁷⁴ found that the height of the first wave even in very low concentrations of sulfuric acid was greater than that for a one-electron reduction. The relations between acidity and height of the first wave obtained by these authors using sulfuric and hydrochloric acids as supporting electrolyte are shown in Tables 25.3 and 25.4.

When uranyl ion is reduced to uranium(III) in acidic solutions, the oxy ion is converted to a simple ion, a process requiring hydrogen ions. That these hydrogen ions must be dissociated and not merely available is illustrated by the polarogram of uranyl ion in 0.2M acetic acid (Fig. 25.7), in which the final wave is poorly developed. However, the first wave, which is the most important in analytical work, is well developed provided there is a trace of acid present to prevent

hydrolysis. It is during the reduction of uranium below the quinquevalent state that the effect of hydrogen-ion deficiency is manifested.

In many nearly neutral solutions an intermediate wave of varying height, shape, and half-wave potential is frequently observed between

Table 25.3—Effect of Concentration of Hydrochloric Acid on the First Diffusion Current*

Concentration of HCl, normality	Current, $\mu\text{a}/\text{millimole}\dagger$
0.01	4.28
0.1	4.28
0.5	4.28
1.0	5.41
2.0	7.41
6.0	8.56

*One millimolar uranyl sulfate, 0.001 per cent gelatin.⁷⁴

$\dagger$ Measured at -0.4 volt (S.C.E.) and corrected for residual current. Capillary characteristic, $-2.8 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ at -0.5 volt (S.C.E.).

Table 25.4—Effect of Concentration of Sulfuric Acid on the First Diffusion Current*

Concentration of H_2SO_4 , normality	Current, $\mu\text{a}/\text{millimole}\dagger$
0.02	4.77
0.1	5.70
0.2	6.27
0.4	6.70
0.5	7.27
1.0	7.55
1.5	7.69
2.0	7.55

*One millimolar uranyl sulfate, 0.001 per cent thymol.⁷⁴

$\dagger$ Measured at -0.4 volt (S.C.E.) and corrected for residual current. Capillary characteristic, $-2.8 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ at -0.5 volt (S.C.E.).

the two waves already discussed. Since this wave is probably due to the direct electrolytic reduction of a quinquevalent oxygenated intermediate to a quadrivalent ion, it is not surprising that it is greatly affected by variations in the pH.

Many maximum suppressors and complex-forming agents such as phosphate influence the waves; these will be considered later.

Uranyl Waves in Alkaline Mediums. Uranyl ion precipitates partly as hydrous uranyl oxide and partly as a basic salt even at a pH of 5. Harris¹⁸ found no polarographically detectable amount of uranyl ion in solution after the addition of 1.6 moles of sodium hydroxide per mole of uranyl ion.

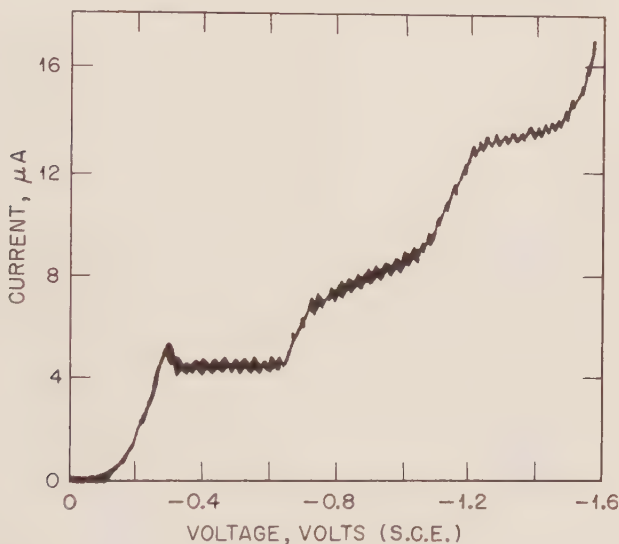


Fig. 25.7—Polarogram of 10^{-3}M uranyl chloride in 0.2M acetic acid, 5×10^{-4} per cent thymol.

However, uranyl ion remains dissolved in alkaline solutions in the presence of complexing ions such as tartrate, citrate, or carbonate. Polarograms^{18,19} of uranium(VI) ion in these solutions generally consist of a fairly well-shaped one-electron reduction wave in the region of -0.7 to -1.1 volts (S.C.E.). This wave is sometimes followed by a second, more drawn-out wave, which is of equal height or somewhat smaller. In 0.1N sodium carbonate a single one-electron reduction wave with a half-wave potential of -1.1 volts (S.C.E.) is obtained. If the sodium carbonate concentration is increased to 1N , the half-wave potential shifts to -0.9 volt, but the wave is not so well shaped. In 0.1N to 0.5N ammonium carbonate the first wave due to a one-electron reduction is well shaped and has a half-wave potential of close to -0.9 volt (S.C.E.). The polarogram contains a second smaller wave whose height approaches that of the first as the concentration of ammonium

carbonate increases. Presumably the shift in the first reduction wave after the solution is made alkaline results from the fact that the uranium ion which is reduced is present either as a complexed anion or at a lower pH as UO_2OH^+ , since hydrogen ions are not available. The second wave which appears in some alkaline mediums is probably due to the reduction of a uranium(V) oxy complex to a uranium(IV) oxy complex. Alkaline supporting electrolytes have found little application in the polarographic determination of uranium.

Table 25.5—Table of Uranium Polarograms

No.	Supporting electrolyte	Electrode reaction	Half-wave potential vs. S.C.E.	Sensitivity (I)*	Remarks	Reference
U(VI)						
1	0.1N HCl	U(VI) U(V)	-0.183	1.54	Similar from 0.01N to 0.2N HCl	18
2	2N HCl	U(V) U(III)	-0.94	3.08	Similar above 2N HCl	18
		U(VI) U(IV)	-0.213			
3	0.1N H ₂ SO ₄	U(IV) U(III)	-0.9	2.0	Intermediate small wave brings total of first two waves to two-electron change; acid concentration fairly critical	88 74
		U(VI) U(IV)	-0.22			
		U(V) U(IV)	-0.9	2.35		
		U(IV) U(III)	-1.06			
4	1N H ₂ SO ₄	U(VI) U(IV)	-0.19	2.72	Second wave nearly masked by H wave	74
5	0.5M oxalic acid	U(VI) U(IV)	-0.13	3.2†	Well-shaped wave; no additional waves before -0.9 volt	18
6	0.2M potassium oxalate	U(VI) U(V)	-0.44	1.57†	Well-shaped wave; no additional waves before -1.7 volts	18
7	2M hydroxylamine hydrochloride	U(VI) U(V)	-0.28	2.07	Good supporting electrolyte; Fe wave eliminated	18 88
		U(VI) U(V)	-0.27	2.02		
8	0.2M acetic acid	U(VI) U(V)	-0.21	1.7†	Second wave too small and poorly shaped	18
		U(V) U(IV)	-0.7			
		U(IV) U(III)	-1.15			
9	Citrate buffer: 0.1M potassium citrate, 0.1M citric acid	U(VI) U(IV)	-0.38	2.4†	Appears to be two nearly coalesced waves with half of -0.30 and -0.43 volt; no additional waves before -1.4 volts	18
10	Pyridine buffer: 0.1M pyridine, 0.1M pyridine hydrochloride	U(VI) U(V)	-0.4	1.5†	First irregular and drawn out; second drawn out	18
		U(V) U(IV)	-1.1			
11	Mixture of acids: 0.1M phosphoric acid, 0.1M hydrochloric acid	U(VI) U(V)† U(IV)	-0.2	2.2†	Current decreases to minimum between -0.8 and 1.3 volts	18

Table 25.5—(Continued)

No.	Supporting electrolyte	Electrode reaction		Half-wave potential vs. S.C.E.	Sensitivity (I)*	Remarks	Reference
U(VI)							
12	0.1M ammonia	U(VI)	U(V)	-1.0	1.6†	At second wave develops -1.3 volts with increase in salt	18
13	-0.5M ammonium carbonate	U(VI) U(V)	U(V) U(IV)	-0.83 -1.45	1.5†	At conc. only fair -1.3 volts diff. currents	18
14	0.1M sodium carbonate	U(VI)	U(V)	-1.13	1.4†	At one wave -1.4 volts	18
15	1M sodium carbonate	U(V)	U(IV)	-0.95	1.5†	One wave; slow rise	18
16	0.1M sodium hydroxide	U(VI)	U(V)	-0.71	1.0	Drawn out	18
	0.1M ammonium citrate	U(V)	U(IV)	-1.34	1.8		
17	1.0M sodium hydroxide, half-saturated ammonium tartrate	U(VI) U(V)	U(V) U(IV)	-0.67 -0.8 to -1.6	1.1	Continuous increase after -0.8 volt	18
18	1M hydroxylamine hydrochloride, 5 per cent tartrate			-0.35	2.41		88
19	50 per cent diammonium citrate			-0.35	1.21	Cu, Fe, Mo, V, Ti, and Pb do not interfere	88
20	50 per cent diammonium citrate, about 0.3M phosphate			-0.48	1.04		88
21	0.1M sodium bitartrate, 0.3M phosphate			-0.25 -0.25	2.13 1.75		88
22	0.1M potassium chloride			-0.19	2.20		88
23	0.1N potassium sulfate			-0.33	1.4		88
24	About 0.01M HF			-0.21	2.48		88
25	0.01M NaF			-0.21	1.84		88
26	1.0M NaF			-0.94	1.4		88
U(IV)							
27	0.1N perchloric acid	U(IV)	U(III)	-0.93	1.62		18
28	0.1N acetate buffer, pH 2.5-4	U(IV)	U(V)	-0.20		Anodic wave	18
U(III)							
29	0.1N HCl	U(III)	U(IV)	-0.93		Anodic wave	18

*See Sec. 2.

†Based on only one polarogram.

The essential data on the polarography of uranium in various supporting electrolytes are collected in Table 25.5. The diffusion currents in some of the buffered solutions may be unreliable.

Uranium(V) Waves. Uranium(V), although an important intermediate in the polarography of uranium, never reaches appreciable concentrations in aqueous solutions because its salts disproportionate into uranium(IV) and uranyl ion until the equilibrium concentration of about 10^{-6} M uranium(V) is reached. Accordingly, no polarographic waves have been obtained with uranium(V) as the original electrolyzable substance. However, waves due to the step-by-step reduction of an intermediate uranium(V) are sometimes observed.

Uranium(IV) Waves. The uranium(IV) wave due to the reduction to uranium(III), Fig. 25.6, corresponds closely to the final uranyl wave for the same reduction. Obviously, a difference in the magnitude of the currents can be expected because two different species are diffusing to the electrode. The half-wave potential is approximately -0.94 volt (S.C.E.) in 1N hydrochloric or perchloric acid and -1.10 volts (S.C.E.) in 1N sulfuric acid. The potential shift in sulfuric acid, which is due to complex formation, is also observed potentiometrically with a mercury electrode.

No anodic oxidation uranium(IV) waves were obtained by Harris¹⁸ or Heal¹² using either the dropping-mercury electrode or the micro platinum electrode. Practically no electrolytic oxidation of uranium(IV) takes place even in large electrolysis cells, although oxidation by chemical methods occurs quite readily. This fact, together with the formation of an unstable uranium(V) during electrolysis, makes the problem of determining standard potentials especially difficult. It should be mentioned that polarographic waves involving the addition or loss of oxygen by cations during the electrolysis are frequently irreversible.

Nevertheless, anodic waves in which uranium(IV) is oxidized to uranium(V) have been obtained in buffered acetate solutions by Tishkoff and Dounce.⁷⁰ In 0.1M acetate they observed that the half-wave potential was close to -0.2 volt (S.C.E.) in the pH range 2.5 to 4 and then became more negative as the pH was increased to about 5.5. Without rigorous proof of reversibility, they correlated the half-wave potentials for the uranium(IV) oxidation and the uranyl cathodic reduction with the potential of the uranium (VI)/(IV) couple. It is interesting that the correlation was that expected for reversible reactions. They also calculated formulas for the various acetate complexes on the basis of half-wave potential shifts. Although no practical application of the uranium(IV) anodic oxidation wave has been made in analytical chemistry, this possibility does exist.

Uranium(III) Waves. Polarograms of pure uranium(III) ion have never been obtained owing to the instability of this ion in aqueous solution. It reacts rapidly with dissolved oxygen and very slowly oxidizes water with evolution of hydrogen. However, Heal succeeded in obtaining a mixture of uranium(III) and uranium(IV) by electrolytic reduction in dilute acid solutions at a mercury cathode. He then obtained a continuous anodic-cathodic wave in the acidic mixture of uranium(III) and uranium(IV) as a result of anodic oxidation of uranium(III) followed by cathodic reduction of uranium(IV). The fact that the wave was continuous and the half-wave potential was the same as that of the uranium(IV) reduction wave proved the electrode reaction



to be at least nearly perfectly reversible. He analyzed the wave and found the coefficient of the logarithm term of the Nernst equation to be 0.06. Harris, who did not study the uranium(III) anodic wave, concluded that the reaction for the reduction of uranium(IV) was not reversible since he obtained a value of 0.08 upon analyzing the uranium(IV) wave. As would be expected from comparison with the uranyl waves, no polarographic reduction wave is obtained before the hydrogen wave.

(b) Commonly Used Supporting Electrolytes and Interferences.
Mineral Acids. In determining the uranium content of solutions with no interferences, the one-electron uranyl reduction wave in 0.1N to 0.5N hydrochloric acid or the two-electron uranyl reduction wave in 1N to 2N sulfuric acid, both measured at about -0.3 volt (S.C.E.), have found the most frequent use. The diffusion currents in either of these acids are essentially constant in the above acid-concentration range. The latter has the advantage of twice as great a sensitivity. It is evident that any ion reduced below -0.4 volt (S.C.E.) interferes. The most serious of these interferences are iron(III), copper, lead, molybdenum, titanium, and vanadium.

Some care must be exercised in the choice of maximum suppressors because uranyl polarograms may be altered as a result of complex formation. Gelatin, 0.001 to 0.005 per cent, has been found to be a satisfactory maximum suppressor⁷⁴ and is superior to methyl red or methyl cellulose.⁸⁴ Caffeine has been used^{18,89} without detrimental effects in concentrations as great as 1 per cent. Thymol 0.0001 to 0.002 per cent is a satisfactory maximum suppressor, but, owing to complex formation, 0.001 per cent thymol causes a definite decrease in current of 1 millimolar uranyl ion, and 0.1 per cent thymol changes the wave shape completely.¹⁸ Gum arabic in concentrations of 0.1 per

cent resulted in the separation of the first uranyl wave in sulfuric acid into two waves of equal height. Apparently the disproportionation of uranium(V) is inhibited; therefore the second wave with gum arabic present is due to the electrolytic reduction of uranium(V).⁷⁴

Hydroxylamine Hydrochloride. If the uranyl solution is made 2N in hydroxylamine hydrochloride and warmed to 50°C for 45 min or boiled for 3 min, iron is reduced to the bivalent state, and its interference is eliminated.^{68,83} Molybdenum, copper, and vanadium interfere in this medium.

Hydroxylamine Hydrochloride - Sodium Tartrate. According to Haight,⁸³ interference of molybdenum and titanium can be eliminated by adding an equal volume of 10 per cent sodium tartrate. The interference of vanadium, which yields a drawn-out wave beginning at zero volt (S.C.E.), remains. The uranyl wave coalesces with either that of copper or lead depending on the pH. At a pH of 2.7 the copper and uranyl waves coalesce, and at a pH of 5 the lead and uranium waves coalesce. Of the maximum suppressors, gelatin, methyl red, and methyl cellulose, Haight found 0.0015 per cent gelatin to be far more effective than similar concentrations of the other two.

Ammonium Citrate. Haight⁸³ obtained three distinct successive waves for copper, uranyl, and lead in 50 per cent ammonium citrate if the pH was kept between 4 and 5. In more acidic solutions the uranyl and lead waves coalesce, whereas in more alkaline solutions the uranyl and copper waves merge. However, the pH is easily kept within the proper range. The iron(III) wave that coincides with the copper wave does not interfere unless there is a large excess. Molybdenum, titanium, and vanadium waves do not interfere since they follow the lead wave. However, phosphates form a complex with uranyl ion causing the uranyl wave to coalesce with that of lead. As a consequence either lead or phosphate must be absent. Methyl cellulose, 0.002 per cent, can be used as a maximum suppressor.

Sodium Bitartrate.⁸³ In 0.1M sodium bitartrate, separate waves are obtained for copper, uranyl, and lead, and there is no interference due to phosphate. However, both the molybdenum and titanium waves interfere. Methyl cellulose, 0.002 per cent, can be used to suppress maxima.

(c) Catalytic Nitrate Wave. The catalytic nitrate wave is of interest because it represents a possible method for determining the very small concentrations of $1 \times 10^{-8}\text{M}$ to $5 \times 10^{-5}\text{M}$ uranyl ion. However, owing to the large number of interferences, this method has found very limited use. In particular many polyvalent cations and ions that form complexes with uranium interfere. No polarographic wave for

the reduction of nitrate is obtained before -2 volts (S.C.E.) in neutral, alkaline,^{90,91} or moderately acidic solutions.¹⁸ However, in the presence of an excess of polyvalent cation a catalytic polarographic reduction wave occurs at as low as -1.0 volt (S.C.E.). Tokuoka and Ruzicka^{90,91} observed a nitrate wave with a half-wave potential of about -1.2 volt (S.C.E.) in a supporting electrolyte of $0.1N$ lanthanum chloride and other salts. About a fiftyfold excess of lanthanum ion was required to obtain the maximum current.

Harris¹⁸ observed that concentrations of uranyl or uranous ion approximately equal to that of the nitrate had an effect similar to that of lanthanum. He observed that the nitrate was reduced at the same potential as the uranous or the second uranyl wave, namely, about -1.0 volt (S.C.E.). On the basis of several experiments he suggested the application of the phenomena to the determination of low concentrations of uranium with an excess of nitrate and mentioned the limitation in that the diffusion current must be measured at about -1.2 volts (S.C.E.) where many other ions interfere. Kolthoff, Harris, and Matsuyama⁹² studied the variables influencing the wave for determining nitrate with an excess of uranyl ion present.

Crompton, Tichenor, and Young⁹³ studied the variables in the uranium determination more extensively and concluded that the method was suitable for the determination of 0.008 to 1.1 ppm of uranium but only with most other ions absent.

A plausible mechanism⁹⁴ for the reduction is that uranyl nitrate complex ions diffuse to the surface of the drop and are reduced to ammonium ion thus:



It appears that there is no appreciable potential barrier to the passage of electrons between the nitrogen in the complexed nitrate and the quadrivalent uranium ion. As a result, when the electrode potential is sufficiently high to reduce the quadrivalent uranium ion, the nitrogen is also reduced. Also, the complex may be held close to the electrode by polar forces during its reduction in a manner comparable with colloidal surface adsorption phenomena. As a consequence, additional free nitrate ions may replace nitrates that have already been reduced, and they may in turn be reduced. It seems reasonable that with large nitrate concentrations the current may then be limited not by the usual polarographic diffusion but by the rate at which additional nitrates can enter the complex that is being reduced. It is evident from Eq. 12 that the concentration of nitrate, uranyl, or hydrogen ion can

be the current-limiting factor. Which of these factors is current-limiting determines the importance of other species of ions. The three cases will accordingly be considered separately.

General Interferences. In solutions more highly acidic than about 0.1N the hydrogen wave interferes. However, the acidity must be sufficient to prevent the precipitation of uranic oxide and to furnish hydrogen ions for the electrode reaction. The acidity can be adjusted just to the acid color of methyl red, 0.0001 to 0.0002 per cent, which also serves as a maximum suppressor. Maximum suppressors, such as thymol, which complex uranyl ion must be avoided.

Previously discharged cations in large concentrations interfere owing to their waves and may also decrease the nitrate wave height. Phosphates interfere by precipitating uranyl ion. They can be precipitated as alkaline-earth phosphates. The interference of complex-forming ions is discussed for the separate cases.

Case 1. Hydrogen-ion Concentration Is Current-limiting. At very low acidities the rate of diffusion of hydrogen ions and consequently the hydrogen-ion concentration can become current-limiting since 10 hydrogen ions are consumed for each nitrate reduced in the electrode reaction. It is evident that the hydrogen-ion concentration should be kept much larger than that of the nitrate actually responsible for the current. It has been shown⁹² that 0.02M to 0.03M hydrogen ion is sufficient even for the maximum current, yet the hydrogen wave does not interfere. The possibility of determining hydrogen-ion concentrations by this method is of no practical importance.

Case 2. Uranyl-ion Concentration Is Current-limiting. Provided the hydrogen-ion concentration is sufficiently large and the nitrate concentration is kept large and constant, it is possible to obtain a nitrate reduction wave whose height is proportional to the concentration of uranyl ion. Harris¹⁸ used a supporting electrolyte of 10^{-3} M potassium nitrate, 0.1M potassium chloride, and 0.01M hydrochloric acid and observed a nearly linear relation between the current at -1.2 volts (S.C.E.) and the uranyl-ion concentration from 3×10^{-7} M to at least 2.6×10^{-5} M. The diffusion current was about $4.50 \mu\text{a}$ for 10^{-5} M uranyl using a capillary with a characteristic of $2.64 \text{ mg}^{2/3} \text{ sec}^{-1/2}$. Crompton, Tichenor, and Young⁹³ determined uranium in the range of 1×10^{-8} M to 5×10^{-5} M by using a supporting electrolyte of 0.03M sodium nitrate, 0.02M nitric acid, 0.005M sodium chloride, and 0.0002 per cent methyl red. The diffusion current was $102 \mu\text{a}$ for 10^{-5} M uranyl ion, using a capillary with a characteristic of $2.03 \text{ mg}^{2/3} \text{ sec}^{-1/2}$.

As would be expected, anions interfere in proportion to their tendency to form complexes with uranium. In concentrations of 0.005M the following effects due to anions were observed: Fluoride and oxa-

late eliminate the wave, but oxalate itself causes another wave. The compound ethylenediamine also eliminates the wave due to complex formation. Sulfate, phosphate, and perchlorate cause a serious reduction in the wave height. Tartrate, acetate, and chloride produce a small reduction. The perchlorate interference is difficult to explain since perchlorate forms few complexes.

Large concentrations of cations also interfere. The use of calcium nitrate instead of sodium nitrate in the supporting electrolyte caused a 69 per cent reduction in current, whereas the use of aluminum nitrate resulted in an 84 per cent decrease.

With relatively large uranyl-ion concentrations the wave sometimes contains a minimum, but the current remained proportional to the concentration.

Case 3. Nitrate-ion Concentration Is Current-limiting. If the hydrogen-ion and uranyl-ion concentrations are kept large relative to the concentration of nitrate, the rate of diffusion of the nitrate in the form of a complex becomes current-limiting and can be used as a method for determining nitrates. Kolthoff, Harris, and Matsuyama⁹² measured the diffusion current at -1.2 volts (S.C.E.) using a supporting electrolyte containing $2 \times 10^{-4}M$ uranyl chloride, $0.1M$ potassium chloride, and $0.01M$ hydrochloric acid. Using a capillary with a characteristic of $2.58 \text{ mg}^{2/3} \text{ sec}^{-1/2}$, they obtained a diffusion current of $35.6 \mu\text{a}$ per millimolar concentration of nitrate in the range of $10^{-5}M$ to $5 \times 10^{-4}M$.

From the experimental data of these authors this value is observed to remain constant until the nitrate-ion concentration equals or exceeds that of the uranyl ion by as much as three times, depending on the uranyl-ion concentration. This is rather surprising because the instability constant for any uranyl nitrate complex must be large enough so that all the nitrates would not be expected to be associated with one-third to one-fourth their number of uranyl ions. It is probable that only part of the nitrates are associated and the others are successively reduced. With greater excess concentration of nitrate the current increase is probably limited by the rate of replacement of reduced nitrates in the complex.

In case 3 sulfates interfere only if present in excess above 1 millimolar because the sulfate is less strongly complexed than the nitrate. With the large concentration of uranyl ion used, the nitrates are quantitatively complexed even though sulfates are present.

2.3 Electrolytic-Polarographic Method. On the basis of standard potentials already presented in this chapter, it follows that the electrolytic separation of uranium as a metal is not feasible but that the element can be electrolytically reduced at a mercury cathode to a

mixture of uranium(III) with some uranium(IV), which mixture can be titrated. The separation of other metals by electrolysis into a mercury cathode was used.

3. CONDUCTOMETRIC METHODS

The principles and techniques of conductometric methods of analysis are treated in monographs by Britton,⁹⁵ Boettger,⁸ Sand,³ MacInnes,⁴ Kolthoff and Laitinen,² and Jander and Pfundt.⁹⁶ Instruments are discussed by Reilly and Rae.⁵

Although various types of conductivity and transport experiments have contributed to the chemical knowledge of such properties of uranium compounds as hydrolysis, complex formation, and solubility in organic solvents, attention in this volume is directed to the measurement of conductivity as an analytical tool. The procedure may consist of a single measurement of the conductivity to determine the total ion concentration, or successive conductivity measurements can be made to follow the change of conductivity upon the addition of a reagent as in conductometric titrations.

Conductivity is not specific for any ion since all ions present contribute in an amount depending on their mobility. However, if the solution contains only the electrolyte to be determined or if only an approximate total ion concentration is required, a single conductivity measurement may contribute results that are as valuable as would otherwise be obtained by a long, involved procedure. The conductivity method is used for testing the purity of water or for measuring the concentration of solutions. Usually a working curve is prepared for a particular cell by plotting for several solutions of known concentration the conductivity vs. the concentration. The method is used less frequently for titrations in which there is a change at the equivalence point in the slope of the curve for conductivity vs. volume of reagent.

Apparatus. Bridges are available which are capable of measuring conductivity with an accuracy of better than ± 0.01 per cent, while the temperature can be maintained constant within $\pm 0.001^\circ\text{C}$. Since this precision has been unnecessary in the Project analytical work, less expensive apparatus has been used.

For most purposes circular slide-wire bridges together with a vacuum-tube oscillator and amplifier and headphones can be used in the classical Wheatstone-bridge arrangement. A precision of 0.2 per cent is easily attained even with considerable external noise. The vacuum-tube oscillator is probably superior to the older mechanical oscillator. The shape of the wave produced by the oscillator is easily checked on an oscilloscope.

Conductivity cells designed with electrodes varying from 1 or 2 mm apart for very pure water to several centimeters apart for electrolytes of low resistance are commercially available. Dip electrodes for immersion into containers are useful for many tests. This convenient and easily used type of electrode assembly is furnished with several commercial conductivity-measuring instruments. Pyrex glass is sufficiently insoluble for most analytical work.

Conductivity cells of special design can easily be constructed from pyrex glass and platinum sheet and wire. One micro conductivity cell consisting of bright platinum electrodes 1.5 mm in diameter and 1.5 mm apart yielded easily reproducible results using as little as 25 microliters of solution. The cell constant was 2.4 per centimeter. The electrode leads, which passed through the bottom of a small pyrex cone, were about 0.04 mm in diameter. Details of this cell are described by Watters and Sheel⁹⁷ as used in the conductometric determination of traces of carbon (Fig. 25.1).

Kraus⁹⁸ in studies that were primarily theoretical found that pure solutions of uranyl nitrate could be as accurately determined by a single conductivity measurement as by classical gravimetric or volumetric methods, namely, to ± 0.2 per cent. He washed the sample into a conductivity cell diluted to 100 ml in volume with conductivity water having a specific conductivity of 1×10^{-6} ohm and measured the conductivity in an oil thermostat at $25 \pm 0.004^\circ\text{C}$.

MacInnes and Longworth⁴⁴ as well as Kraus⁹⁸ studied the phase diagrams and hydrolysis of aqueous uranyl salt solutions by conductivity and pH measurements.

Mundy⁹⁹ determined the conductivity of a solution of uranyl nitrate in diethyl ether. He observed that the conductivity was only about one-thousandth as great as that of an aqueous solution. The equivalent conductance decreased with dilution, an effect frequently observed in organic solvents having dielectric constants of less than 12. Mundy and Furman¹⁰⁰ applied conductance titration to the determination of nitric acid in uranyl nitrate solutions.

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Chapter 26

SPECTROCHEMICAL METHODS

By M. Fred and B. F. Scribner

This chapter consists of a general discussion of spectrochemical methods, descriptions of the fundamental principles on which they are based, indications of the reasons for the adoption of each method, and comparison of their effectiveness for different problems.

Spectrochemical methods of analysis provide for the detection and determination of chemical elements in materials by observation of their emission spectra. Each of the chemical elements can be made to emit a characteristic spectrum; consequently, each element can be determined, although the ease of observation varies considerably among the individual elements. By convenient procedures involving arc and spark excitation 70 elements may be detected at low concentrations in a wide variety of materials. The remaining elements, mostly gases and metalloids, require special procedures for their observation; in general, no advantage is offered by the spectrochemical determination of these elements over established chemical methods. Applications of spectrochemical methods to quantitative analysis have been a comparatively recent development resulting from refinements attained in spectral excitation, photography, and photometry in the past twenty-five years. The basic principles of qualitative and quantitative analysis have been adequately presented in treatises on the subject.¹⁻³

Spectrochemical methods of analysis have proved to be particularly well suited to many of the desired analyses. This condition is due to the fact that by these methods the impurity levels of many elements can be simultaneously determined with great sensitivity and with moderate though sufficient accuracy. It is fortunate from the standpoint of availability of equipment that the popularity of spectrochemical methods throughout the country in general has recently exhibited

a remarkable growth. However, developments outside the Manhattan Project have been concerned mostly with the determination of alloying constituents and of impurities present in appreciable rather than trace amounts in metals, with emphasis on the highest possible accuracy.

Table 26.1—Typical Sensitivity Limits

Element determined	Carrier-distillation method; impurity in 100 mg of U_3O_8 , ppm	Copper-spark method, m γ *
Ag	0.05	
Al	5	10
As	5	500
Au	0.03	20
B	0.01	10
Ba	10	10
Be	0.1	0.2
Bi	0.5	20
Ca		2† (0.1)
Cb		20
Cd	0.07	200
Ce		50
Co	1	50
Cr	3	5
Cs	8	50
Cu	0.3	
Dy		50
Er		50
Eu		2
F		10
Fe	1	50
Ga		100
Gd		10
Ge	0.2	
Hf		50
Hg	10	500
Ho		20
In	0.5	100
Ir		500
K	2	10
La		5
Li	0.1	0.2
Lu		200
Mg	0.5	1† (0.1)
Mn	1	2

Table 26.1 —(Continued)

Element determined	Carrier-distillation method; impurity in 100 mg of U_3O_8 , ppm	Copper-spark method, m γ *
Mo	1	5
Na	0.5	10†
Nd		20
Ni	2	10
Os		
P	50	2,000
Pa		200
Pb	1	5
Pd		50
Pr		20
Pt		2
Pu		500
Ra		10
Rb	1	20
Re		200
Rh		
Ru		100
Sb	10	500
Sc		0.5
Si	3	10
Sm		20
Sn	1	
Sr		50
Ta		100
Tb		
Te		50
Th		20
Ti		10
Tl	3	
Tm		5
U		100
V	5	5
W		50
Y		1
Yb		10
Zn	20	200
Zr		10

*1 m γ = 10^{-9} g.

†Denotes limit set by contamination. Values in parentheses are estimates of what the limit would be with no contamination.

A large number of the spectrochemical analyses performed have consisted in tests on uranium samples. The specifications for the purity of the metal are quite rigorous in that tolerances are quoted for most of the elements in the periodic table. The tolerances vary in a random manner but are always low, in some instances as low as a fraction of a part per million. Coupled with this difficulty is the fact that the spectrum of uranium is extremely complex, consisting of many thousands of lines of comparatively uniform intensity. In fact, the uranium spark is a well-known source of continuum for absorption spectra under low dispersion. The spectrum of appreciable amounts of uranium excited in a carbon arc is quite brilliant. By conventional methods, therefore, it would be difficult to detect even ordinary amounts of impurities. Fortunately, it has been found possible to develop a procedure, known as the "carrier-distillation method," which makes use of differential volatilization in a graphite arc to effect a separation of volatile impurities from uranium and at the same time to yield remarkable sensitivity for these elements. For the nonvolatile impurities, to which the method does not apply, conventional methods are used, combined with chemical separations when greater sensitivity is required.

The carrier-distillation method is also used in the analysis of other materials that form refractory oxides. The adoption of the method in these instances may be attributed primarily to the complex spectrum of the matrix, as in the case of thorium and the rare earths, or simply to the high sensitivity for impurities in materials such as aluminum, calcium, and beryllium.

Two special methods have been used for the analysis of solutions. In the copper-spark method a hydrochloric acid solution is evaporated on the flat ends of a pair of copper electrodes, which are then excited in a spark. This procedure gives very high absolute sensitivity and can be used for the simultaneous determination of a great many elements, provided the solution is quite dilute and does not attack copper. In the other method, known as the "porous-graphite method," the solution itself is fed into the spark by impregnating a graphite electrode, and the restriction on the composition of the sample is consequently much less. The accuracy is better but the sensitivity much poorer than in the copper-spark method.

As illustrations of the sensitivity attained in the two most commonly used methods, namely, the carrier-distillation method for the analysis of U_3O_8 and the copper-spark method for the analysis of dilute solutions, the lower limits are quoted in Table 26.1. These results were obtained by Scribner¹² for the first method and by Fred³³ for the second method. A Baird grating spectrograph was used in both methods. It should be noted that the first set of lower limits refers to

concentrational sensitivity (parts per million) in a matrix giving complex spectra, whereas the second set refers to absolute sensitivity (weight) in the absence of interfering spectra. Thus the two sets of limits deal with different types of problems and, consequently, are not strictly comparable. The limiting weights in millimicrograms detectable in 100 mg of U_3O_8 may be obtained by multiplying the values in the middle column by 100.

1. EQUIPMENT

1.1 Spectrographs. The cumulative experience of a number of laboratories in developing the spectrographic procedures described in this volume serves to indicate which instrumental features are of particular value in this work. In this chapter the discussion will be based mainly on considerations of general design rather than on a comparison of the quality of construction among different makes, since the latter aspect is transitory and the authors' experience reflects unduly the wartime conditions of manufacture.

The conclusion may be stated immediately that any of the large modern commercial spectrographs is suitable but that certain features are especially important in view of the somewhat peculiar problems encountered. These instruments are now designed primarily for routine spectrochemical analysis in industrial laboratories with greater emphasis on dependability of adjustment, convenience of operation, and freedom from scattered light than in models used for research, in which the resolution is perhaps the main factor for a given type of spectrograph. The present requirements of high sensitivity and complete coverage of the spectrum, on the other hand, put somewhat more emphasis on flexibility, dispersion, and speed.

High dispersion is desirable not only because of the complex spectra often encountered but particularly because of the increased sensitivity gained thereby. The limiting amount of an element that can be observed is reached when its spectrum line cannot be distinguished above the continuous background of the source. Increasing the dispersion reduces the amount of continuous spectrum in the wavelength region in the neighborhood of the line and thus increases the line-to-background ratio. Hence, other factors being equal, the sensitivity is proportional to the dispersion. This relation has been tested repeatedly, and the lower limit observable with a grating spectrograph in the second order has been shown consistently to be half the limit reached in the first order. It should be mentioned that for a comparison of this sort to be valid other effects must not enter, such as would arise with the use of different exposure times with a source in which the line-to-background ratio is dependent upon time.

An upper limit governs the dispersion that may be used because of the reduction in speed of high-dispersion spectrographs. From the standpoint of maximum sensitivity an exposure time falling within the useful volatilization period of the light source should produce a background density on the linear portion of the characteristic curve of the photographic emulsion. If the spectrograph used with a particular source is too far in the direction of high dispersion and low speed, the contrast of a weak line above the low background is poor. The speed required with a weak source, such as the copper spark, is somewhat greater than for the arc source used with the carrier-distillation method.

It has been found that the large commercial spectrographs now available have nearly the optimum combination of speed and dispersion, especially the grating instruments with a dispersion of 5 Å per millimeter in the first order. It is frequently desirable to use such instruments in the second order for the sake of better sensitivity and resolution; hence, it is advantageous to use a grating with a brightness distribution having a broad maximum at about the first-order red. Under these conditions the background densities for first- and second-order ultraviolet are about equal, and the extra intensity in the first-order red and infrared constitutes an advantage because the background intensity of the source is usually somewhat lower in this region and the sensitivity of the photographic plates is poorer. However, this grating distribution is likely to be unfavorable if much work is to be done in the first-order short-wavelength ultraviolet, e.g., Cd 2288, because of the rapid decrease in grating reflectivity and photographic speed as the wavelength is decreased in this region. In general, it may be said that, although the dispersion of the large grating spectrographs is well suited to the procedures described in this volume, the speed has, at best, little extra margin and, in instruments with a poor grating, may even be deficient for some purposes. For a few applications greater speed than is obtainable at present with the same dispersion would be a definite advantage.

The speed of large Littrow prism spectrographs is about equal to the speed of large grating spectrographs, or perhaps slightly higher. The variation in dispersion, however, is a disadvantage since a uniform background is not obtained and the sensitivity is poor for elements that must be observed at long wavelengths. On the other hand, the high dispersion in the ultraviolet is favorable, if observation can be confined to this region.

Among other characteristics of spectrographs that are generally desirable for spectrochemical analysis, the useful wavelength range is particularly important for various applications. This includes the

total wavelength range that can be covered, the range available in a single exposure, and the flexibility with which the latter can be changed over various regions of the total range. The majority of samples must be examined for impurity lines from the ultraviolet to the infrared. Hence, the number of separate exposures required is less for a spectrograph accommodating a 20-in. length of photographic plate than for one handling only 10 in. at the same dispersion. Moreover, if the wavelength region covered is adjustable continuously rather than in large steps, it is sometimes possible to include all the lines of interest in a single exposure instead of the two exposures that might otherwise be required. The type of spectrograph loaded with 100-ft lengths of film is inconvenient if a wide wavelength range, requiring several photographic emulsions with different wavelength sensitivity, is to be covered.

1.2 Standard Spectrographic Accessories. A good deal of accessory equipment is required in any spectrochemical laboratory, and it is unnecessary to describe here standard items such as power sources, densitometers, and darkroom facilities. In general, owing to better engineering and construction, commercial equipment is to be preferred to laboratory-built apparatus unless some special requirement is necessary. Convenient, reproducible, and trouble-free performance is essential.

The standard items manufactured by ARL-Dietert have been found to be generally adequate. Special mention may be made of the comparator-densitometer, whose dual projection system is very useful in comparing sample exposures with standard plates for the identification of elements and semiquantitative determination by visual matching.

1.3 Special Accessories. In addition to the standard items of equipment mentioned above, a great variety of accessories are required for efficient operation because of the nature of the problems encountered in this work.

(a) Chemical Laboratory Equipment. A well-equipped chemical laboratory adjacent to the spectrographic laboratory is needed for the preparation of samples. The space and equipment necessary depend on the number of samples analyzed and on the nature of the preliminary treatment. For example, conversion of uranium-metal samples to oxide for the carrier-distillation method is a matter of an acid wash and ignition over burners or in a muffle furnace, while a chemical separation by precipitation or extraction requires much more bench space per sample. A separate room is desirable for use with the copper-spark method in order to minimize contamination from other operations. The appearance of the rooms should suggest a



Fig. 26.1 — Electrode cutters.

hospital atmosphere in their freedom from dust, achieved by sealing the walls and windows, providing filtered air at positive pressure, storing unused apparatus in cabinets, etc.

The conventional laboratory equipment must be selected with care. Muffle furnaces should be lined with silica muffles that can be removed and cleaned periodically with acid. Stainless-steel tongs must be used with the furnaces, since cadmium-plated tongs are a source of cadmium contamination. Silica ware is widely used to eliminate boron contamination, and platinum ware is used to eliminate silicon. Mortars and pestles, employed for preparing oxide samples, must likewise be chosen with care. Agate and polished mullite are usually satisfactory, but they introduce silicon or aluminum in the samples. Stainless steel eliminates this difficulty at the expense of iron contamination, and the surface soon dulls and scratches. Tungsten carbide or titanium carbide is probably better for this purpose.

(b) Electrode Preparation. Graphite electrodes are fabricated for the carrier-distillation method and for qualitative procedures according to specifications by sawing into $\frac{5}{8}$ -in. lengths and drilling both ends. Commercial electrode shapers now available are not suitable, because they will not accommodate such short lengths, but the basic design is easily modified to avoid this difficulty. Figure 26.1 is an illustration of an assembly constructed at the National Bureau of Standards, consisting of a motor with double-ended shaft, with a jeweler's slotting saw and a drill chuck mounted at one end and a second drill chuck mounted at the other end, each with appropriate guides. For greatest sensitivity it is essential that provision be made for holding the graphite with filter paper or metal, since fingers or rubber gloves are a source of contamination. A lathe can be used, but it is not so convenient as the special assembly. Upper electrodes are pointed in a pencil sharpener fitted with a stainless-steel adapter to support a $\frac{1}{8}$ -in. rod.

A lathe is necessary for preparing electrodes for the copper-spark method; it should have a lever-type collet chuck. It is possible to shape and position the tool so that turning and facing can be accomplished without changing its orientation.

Machined copper electrodes or loaded graphite electrodes may be supported in plastic blocks drilled with a dozen $\frac{17}{64}$ -in. holes with suitable covers. In one type of construction the holes are surrounded by annular wells to hold inverted sawed-off test tubes.

Solutions are added to electrodes by means of calibrated capillary pipets fitted into tuberculin syringes and are evaporated by standing the electrode in coils of about 10 turns of resistance wire heated by current from an autotransformer.

Dry samples are weighed on a watch glass, to which a small funnel has been sealed near the edge (through which the sample can be brushed into the electrode or die) or, more conveniently, on a small,



Fig. 26.2—Pellet press with insert showing details of pellet die assembly.

pointed metal pan with a direct-reading balance. The die referred to is part of a small pellet press that has been found desirable for some samples; it is shown in Fig. 26.2.

(c) Arc and Spark Stands. The chief requirement for arc and spark stands for Project purposes has been to provide a means of keeping the electrode holders clean, particularly when arcs radiating considerable heat are employed. A satisfactory design is the one developed by Scribner and Corliss.⁴ In addition to many conveniences of adjustment it has water-cooled electrode holders that can easily

be cleaned by wiping with tissue. Similar holders can be constructed to fit into conventional stands. It has been found that chromium plating becomes corroded when used with a graphite arc.

(d) Arc Igniter. The high-frequency igniter described by Brockman and Hochgesang⁵ has been adapted by Tomkins⁶ for use with the rectified d-c arc. The igniter is convenient for striking arcs between graphite electrodes in order to avoid contamination, to maintain proper alignment of the electrodes, and to avoid the possibility of

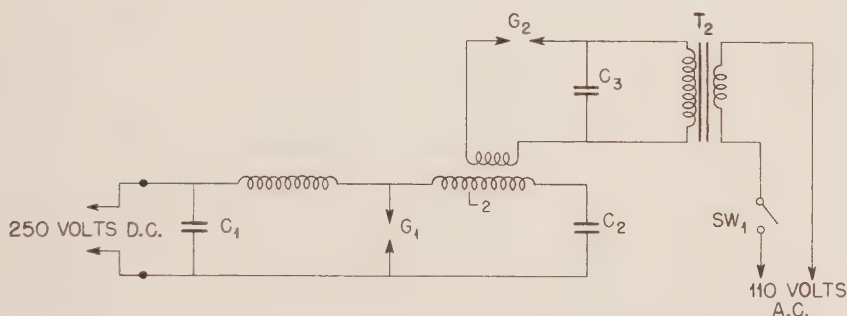


Fig. 26.3—Circuit for high-frequency igniter.

C_1 , 8- μ f 450-volt tubular condenser.

C_2 , 0.01- μ f 35,000-volt condenser.

C_3 , 0.002- μ f 10,000-volt condenser.

L_2 , 26 turns of No. 14 copper wire, $3\frac{1}{2}$ in. in diameter, 5 in. long.

G_1 , analysis gap.

G_2 , auxiliary gap (tungsten-faced contacts $\frac{1}{4}$ in. in diameter).

T_2 , neon-sign transformer, 110/7,500 volts.

SW_1 , momentary-contact push-button switch.

overexposure to the eyes. The igniter is also very useful with an enclosed source, in which the gap cannot be bridged and the electrodes are moved with greater difficulty.

A suitable circuit is shown in Fig. 26.3. The igniter is enclosed in a standard 15- by 21- by $10\frac{1}{2}$ -in. metal cabinet, into which the direct current is fed. High-voltage cables lead from this cabinet to the arc stand and also carry the arc current. The igniter is operated by a push-button switch in a small box connected by flexible leads and located near the arc stand. The cabinet is mounted under the bench supporting the spectrograph, the power cables being about 5 ft long.

It was found that the igniter, when constructed according to the specifications of Brockman and Hochgesang, failed to initiate the arc when used with a rectifier set. It was found by means of an oscillo-

graph that the high-voltage sparks occurred at zero voltage of the pulsating direct current furnished by the rectifier. This defect was remedied by increasing the capacity of C_1 from 0.03 to 3 μ f. It should be noted that essentially the same device is incorporated in the ARL-Dietert Multisource when operated as a d-c power supply.

(e) Intensity Weakeners. Calibrated intensity weakeners have been used not only to measure photographic emulsion contrast but also to extend the range of useful intensity. This range is important for many applications because of the variety of concentrations encountered. Rotating step sectors are most convenient for this purpose. However, sectors are not suitable for use with the copper-spark method if a wide intensity range is to be covered because the number of flashes passing through the smallest openings is too small for good statistics. Attempts have been made to prepare step wedges that are true intensity weakeners and not dependent on time. It may be worth while to report that improvised methods of preparation have been unsuccessful. In attempting to sputter platinum or quartz it was found that the process could not be controlled sufficiently well to yield the desired transmissions, and it was evident that an evaporation process would be even more difficult to control. Photographic wedges were consequently resorted to but were found difficult to calibrate. Wedges exposed on Eastman Spectrum Analysis No. 1 plates show scattering from the finite grain size, revealed by non-additive densities for the different steps when used with the spectrograph, as well as by differences in calibration by the spectrograph and by a spectrophotometer or densitometer. Eastman type 548-O plates (almost grainless) reduced this difficulty, but they were unsatisfactory because of the yellow stain, which has an absorption spectrum with considerable structure.

(f) Aids in Wavelength Identification. Since the possible presence of almost every accessible element has had to be investigated, often in matrices with rather complex spectra, the question of proper choice and identification of wavelengths has been of some importance. A comparison of the compilations of sensitive lines of the elements by different authorities shows many instances of disagreement. These may be ascribed to differences in the method of excitation (electrode material, current density, etc.), in the type of spectrograph (prism or grating, wavelength range covered, dispersion, etc.), in the matrix, and in other factors. Since the highest possible sensitivity has been required, it has been necessary to select the best lines empirically for each procedure by using successively smaller quantities of each element. These wavelengths are listed in the various procedures described in this volume. In general, the best agreement in sensitive

lines for the graphite arc has been found with the lines listed by Gerlach and Riedl.⁷ For determining rare earths by the copper-spark method the sensitive lines listed in the 'Handbook of Chemistry and Physics'⁸ were found most reliable.

The old-fashioned method of identifying lines by wavelength measurement to the second or third decimal place by using a comparator has the disadvantage of being slow; consequently, an eyepiece with a built-in metric scale reading to about 0.01 mm is often used. However, it has been found that if many lines are present, this method can lead to confusion that may not be recognized immediately. A convenient procedure is to prepare comparison plates on which the number of elements present in each exposure is limited to one or two. The comparison plates containing exposures with successively smaller amounts of each element are very useful for analyzing samples with complex spectra for impurities by means of the dual projector of the ARL-Dietert densitometer.

It has been found worth while to prepare wavelength scales reading directly in angstroms for each wavelength region commonly employed, and a simple procedure was devised which used the ARL-Dietert densitometer projection system as a substitute for a dividing machine. A blackened photographic plate (type I-L or I-N) is inserted in one carriage and scratched at positions determined by the projected image of a transparent metric scale mounted in the other carriage. The scale provided with large Littrow prism spectrographs is suitable, and the same scale should be used for measuring the dispersion from an exposed plate. The measurement is also most conveniently made by using the projector. Interpolation between the images of millimeter rulings is facilitated by holding a small scale, suitably divided, on the screen. For a grating spectrograph with a focal length of about 3 meters the dispersion can be assumed as linear over a 10-in. plate, and the positions for integral wavelengths may be calculated on a computing machine. For a prism spectrograph integral wavelengths are read from a large-scale graph of position vs. wavelength of measured lines. The scratching is accomplished by holding a razor blade against a block which is machined to fit closely against the plate clamping bars and which rests on the plate. In operation the block remains stationary against the projector housing as the plate is slid under it by means of the handwheel, the motion being stopped at the predetermined positions as read on the metric scale. The final scale is a contact print of the ruled plate. The whole process for a grating scale can be completed in several hours.

(g) Briquetting Press. For some purposes the ARL-Dietert briquetting press has been found useful. It was found to be economical

in handling samples to replace the $\frac{1}{4}$ -in. (or larger) die and plunger ordinarily supplied with a system having a $\frac{1}{8}$ -in. diameter. The commercial die is made with a 3-deg taper at the top to permit the ejection of the briquet by removing the top and running up the plunger. This means that much of the plunger remains outside the die during the briquetting operation, and a $\frac{1}{8}$ -in. plunger is too easily bent for this sort of system. Accordingly, the plunger was made of such length

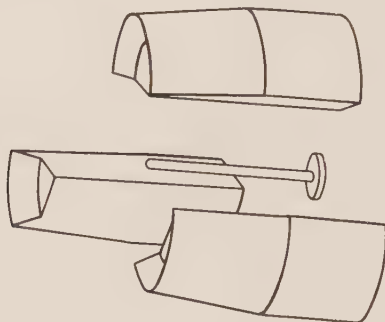


Fig. 26.4 — Die for preparing pellets $\frac{1}{8}$ in. in diameter in a briquetting machine.

that almost all of it entered the die during the briquetting operation, and the briquet was removed by disassembling the die, which was made in three 120-deg sections, as shown in Fig. 26.4. The inside of the die must have a high polish in order to keep the briquet from sticking. Redistilled kerosene is used as a die lubricant.

2. STANDARDS

Spectrochemical methods are, of course, relative methods, based on a comparison of the sample with similar materials of known composition. In view of the unusual nature of the materials and of the analyses required it has been necessary to synthesize the standards as well as to develop the methods for their analysis.

2.1 Dry Standard Samples. As has been emphasized, most of the analyses undertaken have dealt with the determination of traces of impurities. The preparation of a standard containing an impurity of the order of 1 ppm presents several problems in addition to the obvious one of known composition. Among these problems are homogeneity and the reduction of residual impurity in the matrix to a minimum. The problem of matrix purity is discussed below, since it

must be considered in all types of standards, but the problem of homogeneity is peculiar to dry standards.

The samples for which the standards are intended are usually in the form of oxides that have been ignited and finely ground. At a concentration level of 1 ppm the particle size must be of the order of a few microns or less, uniformly dispersed, in order to avoid fluctuations in composition, and the standards must be prepared in such a way as to achieve this order. Three procedures have been investigated: dry mixing, adding solutions of the impurities to the dry matrix and drying, and mixing solutions of all the constituents and drying. The last method is actually the least satisfactory because of the segregation produced on evaporation, but the other methods have both been used with success. For dry mixing, all the constituents are first ground finely and then mixed at a level of about 10,000 ppm. A series of more dilute standards is then made by successive dilutions with the pure matrix, thereby avoiding nonuniformity arising from large dilution factors. Successive dilution of each preceding standard is unnecessary if the standards are prepared by adding solutions to the matrix, the final concentration being regulated by the amount and concentration of the solution added. The solution method is better adapted to the preparation of large quantities of standards, since excessive grinding time would be required by dry mixing. In any case, an automatic mortar grinder is desirable, with the pestle pressure regulated by a spring or counterweight in order to avoid contamination by the mortar.

2.2 Standard Solutions. The preparation of standard solutions is a straightforward process except for very dilute standards of common elements such as calcium or sodium. It has been found convenient to prepare stock solutions of the individual elements at a concentration of 1 mg per milliliter for use with the copper-spark method. Most of these stock solutions are stable for many months, but if a particular solution is not stable, the fact is quite noticeable at this concentration. Adsorption effects may be anticipated at very dilute levels, but they have not been so great as expected over a period of weeks, even for highly charged ions.

Stringent precautions are necessary to minimize contamination by common elements. For example, solutions should be made and handled in quartz apparatus, and the laboratory must, of course, be dust-free.

2.3 Matrix Purification. To satisfy the analytical requirements it is frequently necessary that the standards extend to ranges below the purity level of the samples. This requirement may introduce considerable difficulty. In some cases the purity achieved in large-scale

production may exceed the purity possible in the laboratory in attempting to purify the material for use in standards. In such situations the matrix must be chosen by selection from the materials available. Ordinarily, however, it is possible to devise satisfactory purification procedures if suitable matrix material cannot be obtained. Precipitation (usually by organic reagents), solvent extraction, and sublimation have been found most useful, but other methods may be used as well, and the field is too involved for detailed discussion at this point.

2.4 Standardization. Fundamentally the composition of a standard must be based on chemical analysis, and for the highest accuracy it must be checked by several different methods and laboratories. If high accuracy is not required and no chemical methods of sufficient sensitivity are known, the nominal composition can be assumed, provided it can be demonstrated that no losses or additions due to contamination have occurred in the preparation. For example, the boron content of a standard obtained by evaporation of an acid solution would be doubtful owing to the loss of boric acid.

The question of contamination or residual impurity in the matrix may be answered by an examination of a series of standards of successively lower concentration. The working curve (the graph of log intensity vs. log concentration) should be a straight line with unit slope, provided the concentrations are below the level at which self-absorption in the light source tends to produce saturation. However, if the matrix contains a certain amount of the element as impurity, the working curve must level off at some constant value as the nominal concentration is decreased. (The presence of background intensity will produce the same effect and must be corrected by subtraction from the line-plus-background intensity to give the net line intensity. This correction can be made even for lines as weak as 0.3 to 0.1 of the background, the limit depending on the uniformity of the background and on the precision desired.) The value for the impurity in the matrix may be obtained by the trial-and-error process of adding a constant amount to the nominal concentration of each standard and replotting the working curve. When the proper amount has been chosen for the impurity, the working curve is a straight line. An alternative method is to plot intensity vs. nominal concentration linearly and to obtain the impurity by extrapolation. In the absence of an independent method of analysis no dilute standard should be assumed to be free of contamination until subjected to this treatment. It is apparent that the usefulness of an isolated standard or of a widely spaced series of standards is dubious. If the highest precision

is not required, it is possible, with experience in intensity measurements, to decide the lowest reliable standard by inspecting a series of exposures.

3. SPECTROCHEMICAL METHODS

3.1 Carrier-distillation Method. It has long been recognized that substances are generally volatilized in an arc in the order of their vapor pressures. For example, in 1918 Mott⁹ estimated the boiling points of various metals by observing their differential volatilization from a graphite arc. However, a number of factors besides the volatility of the element influence the rate of volatilization in the arc. If the sample is not present in metallic form, the properties of the compound must be considered. Some compounds, especially halides, are more volatile than the corresponding metals. Oxides, as well as compounds that form oxides on ignition, such as nitrates and sulfates, are usually less volatile and often quite refractory. But even if the compound is volatilized, it is almost immediately decomposed to the metal, as evidenced by the great weakness or, more often, the complete absence of molecular spectra in the arc. Refractory compounds may be reduced before volatilization so that the process is sensitive to the amount of reducing material present. In addition, the rate of volatilization is greatly affected by the presence of other volatile materials in a manner somewhat comparable to the process of steam distillation. Finally, the electrode material affects both the temperature of the arc and the rate of reduction. All these factors must be considered in order to obtain the greatest possible sensitivity.

A procedure rather unfortunately called the "pyroelectric concentration method" has been described in the literature^{10,11} as a spectrochemical method in which the concentrational sensitivity is increased for certain trace constituents by exposing the plate only during the most favorable portion of the life cycle of the arc. Scribner and Mullin^{12,13} considerably extended the effectiveness of this method by using a refractory oxide as the matrix, by providing a carrier for volatile impurities, and by devising a favorable electrode arrangement.

From the standpoint of effectiveness in separating the impurity spectrum from the uranium spectrum it is fortunate that U_3O_8 , to which uranium metal and salt samples can easily be converted, is quite stable with respect to reduction to a more volatile form. On burning in a graphite arc U_3O_8 is reduced to UO_2 , but this oxide is also refractory. Even when the crater of the graphite electrode is burned away sufficiently to expose the oxide directly to the arc, the

uranium is apparently volatilized with difficulty, since it comes off in bursts as the anode spot wanders near it. If powdered graphite is mixed intimately with the oxide, however, reduction takes place easily and the uranium is volatilized uniformly, thus indicating that some control over the reducing power of the arc is possible.

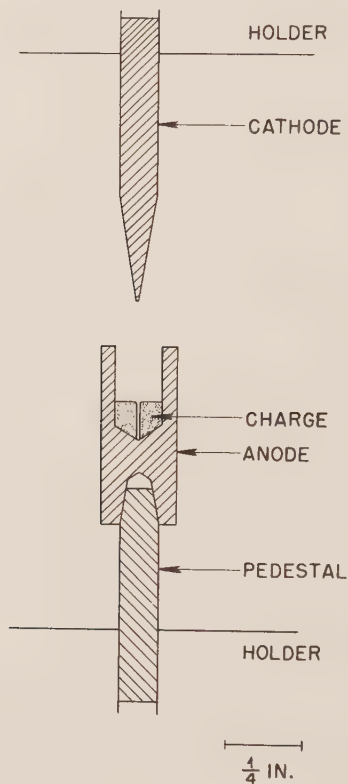


Fig. 26.5—Electrode assembly for the carrier-distillation method.

The electrode arrangement (Fig. 26.5) devised by Scribner and Mullin permits more effective temperature control than is maintained by the conventional method. A short ($\frac{5}{8}$ in.) length of $\frac{1}{4}$ -in.-diameter graphite is used for the anode and is supported by a length of $\frac{1}{8}$ -in.-diameter graphite rod clamped in the electrode holder. The bottom of the anode is drilled with a tapered hole that fits snugly over the tapered end of the post. The sample occupies approximately the bottom quarter of a rather deep ($\frac{9}{32}$ in.) crater with relatively thick

side walls. The electrode is thus fairly well insulated thermally from the holder, and the whole length attains a uniformly high temperature, except for the top surface, which becomes quite hot. The sample is therefore for all practical purposes in a region of rather definite temperature, and the arrangement is much more suitable for emphasizing differential volatility than is the conventional system. If the electrode is made of carbon instead of graphite, a marked temperature gradient downward, caused by the lower thermal conductivity, is noted, and the carrier-distillation process will not function.

The added carrier is perhaps the most important factor in Scribner and Mullin's procedure. If an insignificant amount of material is being volatilized, the arc hisses and is unsteady; and conversely, with volatilization of the sample the arc is quiet and steady and has much less spectrum background. In the latter instance the positive ions supporting the arc are obviously metallic instead of ions of air or carbon compounds, with a corresponding drop in voltage across the arc. The two states are quite distinct, so that the arc is easily recognized as being in one or the other. The quantity of metal vapor required to produce a transition to the quiet state is somewhat critical and is of the order of 0.01 mg. Excess amounts have no effect except to decrease the resistance of the arc and hence to increase the current with a given ballast resistance. A comparison of the spectra from different samples with increasing concentrations of impurity shows an abrupt increase in intensity at the level at which the arc becomes silent.

A more important factor, however, can be seen by a comparison of trace amounts of impurity both with and without added volatile material. The intensity in the former case is many times greater and may be attributed to the impurity vapor swept into the arc by the carrier. After a large portion of the carrier is volatilized, the arc reverts to the hissing state. The behavior of trace impurities in U_3O_8 with 2 per cent Ga_2O_3 added as a carrier is shown in Fig. 26.6, taken from studies by Marshall and Fred,¹⁴ in which intensities are plotted as a function of time after ignition of the arc. The curves for different elements are displaced vertically one unit each to avoid superposition. The dependence on volatility is quite evident. The initial magnesium, silicon, and iron intensity appearing before the gallium is probably due to electrode impurity, but the finite intensity of these elements after the silent period is believed to be due to the sample. It will be observed that iron appears late in the silent period, so that the amount volatilized is quite sensitive to the length of this period. On the other hand, arsenic and boron appear to be completely volatilized before all the gallium. These deductions were verified by col-

lecting the U_3O_8 residues after the end of the silent period, adding more Ga_2O_3 , and repeating the exposures. No boron was found, but the amount of magnesium and beryllium, for example, was practically unchanged. The fraction of the impurity that is volatilized differs widely, therefore, for different elements and has some influence on the sensitivity, although the absolute intensity per atom volatilized is apparently more important. The observed increase of intensity

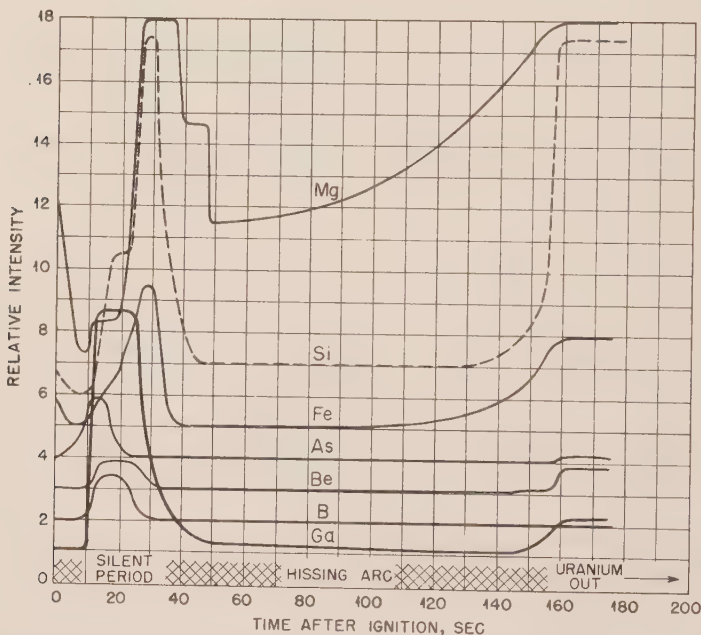


Fig. 26.6 — Spectral intensities as a function of arcing time in the carrier-distillation method.

with increasing concentration of a given element in the sample evidently corresponds to an increase in the absolute rate of volatilization (grams per second), the fraction volatilized remaining almost constant. It might appear, therefore, that the sensitivity could be increased by using greater amounts of carrier. If too much carrier is added, however, the silent period lasts so long that the matrix begins to come out, and a gradual transition from carrier support of the arc to matrix support takes place. Under these conditions it is very difficult to recognize the point beyond which excessive uranium spectrum will be photographed, and a main feature of the method, namely, a

separation of impurity spectrum from uranium spectrum, is lost. There is therefore an optimum amount of carrier.

The selection of the carrier to be used is based on a number of considerations. The carrier, in order to be effective, should be of moderate volatility to provide a steady but not explosive vapor stream, and it should have an ionization potential that is not so low as to suppress the excitation of impurities, in other words, not an alkali. In addition, the element must be one whose impurity level in the matrix need not be investigated (or is otherwise obtainable), it must have a simple spectrum to avoid accidental interferences, and it must be obtainable free from impurities that have to be investigated in the matrix. Gallium oxide, which was originally chosen,¹² is most commonly employed as a carrier. Silver chloride, recommended as a carrier by Harrison,¹⁵ seems to have a slight advantage for the alkaline earths, the other sensitivities remaining about the same, but the uranium background is somewhat higher. Carriers containing a fluoride are effective in increasing the sensitivity of detection of boron.

In the application of the carrier-distillation method it is found that for most of the elements that can be determined the absolute reproducibility is quite good, and an accuracy of about 10 per cent may be obtained by photometric measurement of samples and standards on the same plate. If less accuracy is allowed, as in a "go-no go" type of analysis, comparison with a separate standard plate is permissible, with a considerable gain in speed. The external-standard method, however, yields poor results for less volatile elements, such as iron, which, as observed above, appear late in the silent period and are much more sensitive to fluctuations in the source. Scribner and Mullin¹⁶ showed that greatly improved precision can be obtained for these elements by adding an internal standard, such as chromium, which responds similarly to the fluctuations. The internal standard can be incorporated in the gallium oxide so that no additional labor in sample preparation is required. It should be possible to improve the accuracy for other elements by adding suitable internal standards whenever the extra calibration and densitometry effort is justified.

The electrode charge originally employed for U_3O_8 was 10 mg, an amount that serves satisfactorily when the quantity of sample is limited as in the case of rare materials. In order to obtain higher sensitivity in the analysis of primary uranium-base materials, the electrode charge was increased to 100 mg of U_3O_8 , with appropriate enlargement of the electrode cup to provide optimum volatilization of the charge. The carrier-distillation method has also been applied to the analysis of other refractory materials, such as CaO , BeO , Al_2O_3 , and CeO_2 . Except in the instances of thorium and the rare earths the

advantage lies not so much in the elimination of spectrum interference as in the increased sensitivity as compared with more conventional methods, so that extra labor in converting metals to oxides, for example, is well justified. The procedures have been essentially the same as in the analysis of U_3O_8 , with comparable sensitivities except when smaller samples must be used because of lower density. The situation for CaO and BeO is complicated owing to the fact that the oxide fuses in the electrode and the volatile constituents are not appreciably evolved. This difficulty can be eliminated by mixing the oxide with graphite powder.

The difficulty of sample fusion was also encountered in the case of uranium-columbium alloys containing 1 per cent or more columbium, when gallium oxide was used as the carrier. The method fails completely in that the gallium is not volatilized until after at least a minute of burning, at which time the uranium also comes off, so that no separation is obtained. This difficulty was not expected, since Cb_2O_5 is also refractory. X-ray examination of the material after partial burning showed that the columbium is converted to a carbide, which is not CbC but cannot be otherwise identified and with which the uranium and gallium form a ternary compound (since all three elements must be present for the effect). No difficulty with uranium-columbium alloys is encountered when silver chloride is used as the carrier. Columbium is the only element found to produce this effect.

A minor annoyance in the routine application of the method to the analysis of U_3O_8 was the phenomenon of "popping." In the original procedure the sample plus carrier was brushed through a small funnel into the bottom of the crater of the electrode. A channel for escape of the vapor was provided by punching through the layer of oxide into the graphite with a needle. Occasionally an excessive amount of vapor was generated, and the whole sample would be blown into the arc. This effect could be partially correlated with high humidity and probably also with careless punching, since with experience it seldom occurs. It could also be avoided by drilling a very small hole through the wall of the electrode near the bottom of the crater¹⁵ or by making a pellet of the sample with a small hand press, as shown in Fig. 26.2. The latter procedure, in addition, favors a greater uniformity of background by eliminating small particles of sample that tend to cling to the walls of the crater when the powder is brushed in. However, the sensitivity of detection of impurities is adversely affected, probably because of decreased volatilization from the more compact charge. The pellet procedure improves the reproducibility for low-density samples such as beryllium oxide.

3.2 Complete-burn Method. Elements that are not volatilized in the carrier-distillation method must be determined by other pro-

cedures. If great sensitivity is not required, the sample can be completely volatilized in a graphite arc by the conventional procedure. Pyrophoric metals are volatilized erratically. Hence they are first converted to oxides and mixed with graphite powder to obtain greater uniformity. The difficulty with uranium samples is, as already discussed, the intense background spectrum, so that small samples are used and high dispersion is desirable.

3.3 Cathode-layer Method. A procedure based on the cathode-layer method¹⁷ has been devised by Steadman¹⁸ for the determination of small amounts of uranium in biological materials. By burning the arc in a stream of oxygen to reduce the background and by adding 10 mg of an equal mixture of KCl and $K_2S_2O_7$ to enhance the volatilization, a sensitivity of 0.1 γ was obtained with moderate dispersion. The enhancement factor is stated to be large, and other compounds are said to be effective also, but sufficient information is not available to explain the mechanism. A standard error of about 10 per cent was obtained by adding platinum as an internal standard. Since the performance was not so good in the presence of appreciable amounts of ash, a preliminary ether separation was found advantageous.

3.4 Copper-spark Method. The use of copper electrodes as a support for the evaporation of solutions with subsequent spark excitation has been extensively developed on the Project. The high absolute sensitivity and wide applicability are the two outstanding advantages of the method that have made it ideal for many Project requirements. Copper electrodes have been used in the past with arc sources chiefly to avoid interference from CN bands that are very strong in the violet region when a graphite arc is used. However, because of the relatively poor sensitivity associated with low reducing power for oxide samples, the inconvenience of machining, and the difficulty of maintaining a satisfactory arc with electrodes of low melting point, copper electrodes have not become popular. Gerlach and Riedl¹⁹ used a copper spark in analyzing a radium sample and estimated that they could detect 10^{-10} g of barium in a deposit containing 0.44 mg of radium. This work apparently received no further attention and in fact escaped notice during the early development of the copper-spark method on the Project following its introduction by Rollefson.²⁰

The sensitivity is undoubtedly due to the fact that the sample can be volatilized in the source with a minimum of foreign material from the supporting electrode. The background from the electrode material limits the exposure that may be used; hence the more efficiently the sample can be volatilized during the volatilization of the given amount of electrode material, the greater will be the sensitivity. The advantage of a surface layer of sample in increasing the sample-to-electrode volatilization ratio is obvious. For this purpose an electrode

material such as copper is superior to graphite because it is non-porous, is not so easily attacked by the spark, and has a simpler spectrum. The same argument also applies to the comparison of arc vs. spark because much more electrode material must be consumed by an arc in maintaining the discharge. It will be noted that in this discussion only the relative numbers of atoms are considered, the effectiveness of excitation of the volatilized material being ignored as of secondary importance.

In the development of the copper-spark method it has been found that the sensitivity does not depend critically upon electrical and geometrical variables. Changes in the total power, inductance, electrode gap, etc., affect the brightness of the spark but do not appreciably change the line-to-background intensity ratio for a given amount of sample. Convenience and reproducibility are therefore more important factors, and the procedure used is based on these considerations.

The copper-spark method most nearly fulfills the need for a universal method applicable to almost any sample and in any concentration with a minimum of adjustment. It can be used to analyze a solution for its metallic constituents, or to analyze a more or less pure sample for impurities. The amounts of about 70 elements may be determined simultaneously by the same procedure, and this fact, combined with high absolute sensitivity, makes the method ideal for analyzing minute amounts of samples of widely varying and unusual composition. By special calibration it can be made accurate as well as sensitive. It falls short of being a universal method, however, because of numerous restrictions, such as the amount of acid present other than hydrochloric, the total salt concentration, and other factors.

It will be seen that the copper-spark method is particularly well suited to the widely diverse and difficult analytical requirements of nuclear research work such as was undertaken by the Metallurgical Laboratory. It should be pointed out that great flexibility is essential for these requirements, as contrasted with the usual type of spectrochemical analysis for routine quality control. For example, hundreds of samples of all types of construction materials were analyzed for impurities that might interfere with the operation of a pile. Laboratory equipment and reagents were analyzed for impurities that might influence experimental results, and small quantities of material isolated from various chemical processes were identified and analyzed. In almost all these cases it was necessary to report results at least semiquantitatively so that the effect could be evaluated. The application to the analysis of plutonium, especially during the preliminary small-scale production, is obvious.

Several examples may be cited to indicate how the method is used. Samples of acid are evaporated, and the residues are taken up in a small quantity of hydrochloric acid for evaporation on the electrodes. Compounds to be analyzed for purity are made up in solutions to known concentrations at levels offering the best compromise between sensitivity and spectrum interference. The impurity concentrations in the original sample are obtained as absolute values of each element, thus obviating the necessity of comparison with samples of known purity. This feature is especially important in testing the purity of rare compounds such as rare earths, since only a weighable amount of sample is required (of which only a small fraction is used), and none is required for preparing mixtures of known impurity once the original calibration for each element is made. The method is also well adapted to samples in which a preliminary chemical separation must be made for high concentrational sensitivity, inasmuch as the operations can be carried out on a small scale. A simple operation of this type is electrolytic deposition of the impurity directly on the copper electrodes. Traces of uranium can be concentrated in this way from considerable volumes of salt solutions without evaporation or removal of the salt.

3.5 Porous-graphite Method. Analytical methods based on solutions have the advantage over methods using solid samples that mixtures of known concentration may be made up easily. This advantage more than compensates for the extra labor of preparing solutions of the samples for programs that do not involve large-scale routine testing. A solution method yielding good accuracy has been described by Sloviter and Sitkin²¹ in which the solution is absorbed in a porous-graphite electrode and then vaporized in a spark. The action depends on feeding the solution through the graphite into the spark by capillarity. This procedure was modified somewhat by Fred and Corvin²² and by Dunham²³ so as to yield better sensitivity and reproducibility by immersing the electrode in the solution during the exposure so that it feeds continuously. Greater quantities of solution are thus consumed, and no opportunity occurs for partial drying of the electrode after impregnation. Such partial drying was a variable encountered in the original procedure. These improvements have accrued at the expense of additional labor in preparing the electrodes to fit into the small cups holding the solution and of the requirement for a larger quantity of solution.

The minimum detectable amount of an element is 100 to 1,000 times greater for the porous-graphite method than for the copper-spark method, so that the sensitivity is of the order of conventional d-c or a-c arc sources. The advantages over the copper-spark method con-

sist in greater accuracy and less interference from variations in the composition of the sample. The kind of acid or alkali present is without effect except for attack on the cups in certain instances. However, the cups may be made of any suitable material to withstand attack without affecting the calibration. Relatively large amounts of foreign material can be tolerated, provided they do not give a dense spectrum background, and certain materials may in fact be added as a spectroscopic buffer.

3.6 Silver-briquet Method. The method employing a briquet of a solid sample in a conducting matrix such as silver or graphite was investigated to a limited extent. It was hoped that spark excitation of such briquets made with powders using a large excess of silver would yield a universal method in that previous intensity calibration of a great many elements against silver could be used to analyze quantitatively the composition of any sample. This hope proved to be unfounded, for the intensity for a given amount of an element varied with the type of compound in which it occurred, as shown by Corvin,²⁴ Smith,²⁵ and Tomkins and Holton.²⁶ The effect could be reduced by adding a spectroscopic buffer, especially one containing fluoride, but no direct solution of the difficulty was found. Nevertheless, the method has considerable value for the analysis of samples in which the types of compounds present are known. For samples not easily analyzed in other ways the extra labor involved in a preliminary chemical treatment of the sample in order to control the type of compounds present may be justified.

The applications have included the analysis of iron and aluminum oxide mixtures and the determination of relatively large amounts of refractory oxides in U_3O_8 , good (3 per cent) precision being obtained in special situations without the difficulty of saturation in high ranges, such as occurs with other sources.

3.7 Methods Based on Preliminary Chemical Separation. For some problems it may prove impossible or impractical to devise a direct spectrochemical method, and a preliminary chemical separation is necessary. The separation may be a concentration of impurity from a large amount of sample in order to increase sensitivity; it may involve the elimination of a major or minor component to reduce spectrum background or health hazards; or it may be the substitution of a more suitable matrix. Any of the more selective separation procedures may be used. Solvent extraction of compounds or organic complexes, electrolysis to a mercury cathode, adsorption with an ion-exchange column, and precipitation with a suitable carrier to collect the minor constituent have been found most useful. Such methods are important but are usually employed only as a final expedient,

because the validity of the separation must be established with known samples. However, with the availability of active tracers of many elements a quick check on the separation is often feasible.

Several methods of chemical concentration of impurities in uranium samples have found application. These include a rare-earth

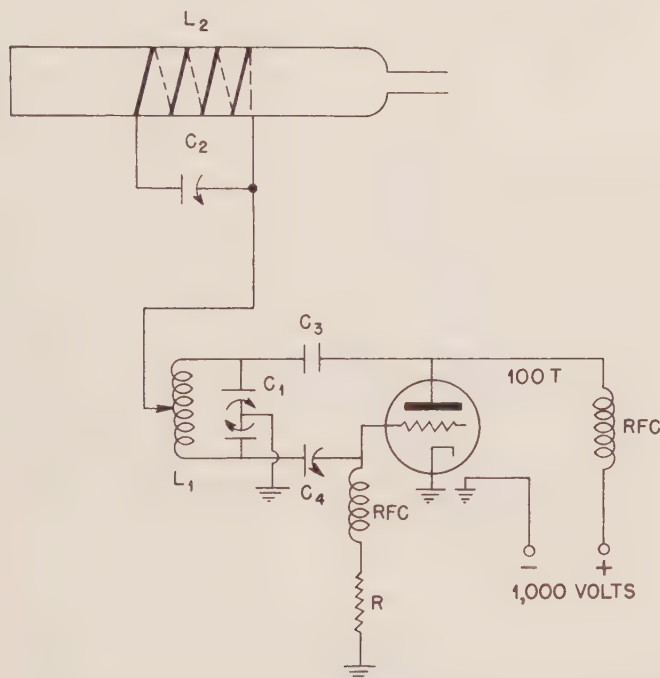


Fig. 26.7—Oscillator circuit for electrodeless discharge. R, 5,000 ohms; L_1 , 7 turns of $\frac{1}{8}$ -in. copper tubing, $1\frac{1}{2}$ in. in diameter, $1\frac{1}{2}$ in. long; L_2 , 10 turns of $\frac{1}{8}$ -in. copper tubing, $1\frac{1}{2}$ in. in diameter, 2 in. long; C_1 , 100 μmf each section; C_2 , 100 μmf ; C_3 , 0.002- μf mica; C_4 , 15- μmf variable; RFC, radio-frequency choke; 100 T, 100-watt transmitting triode.

separation using ether extraction and several peroxide precipitations,²⁷ a concentration of the zirconium group of elements by precipitation and extraction of the cupferrates, with bismuth used as the carrier,²⁸ and a zinc reduction of the platinum group of elements, with gold used as the carrier.²⁹

3.8 Discharge-tube Methods. A small amount of work has been done for special purposes by using gaseous discharge tubes. For the determination of the amount of deuterium in heavy water a conven-

tional electrodeless discharge procedure was employed by Tomkins and Fred,³⁰ the small oscillator shown in Fig. 26.7 being used with a flowing vapor stream. A procedure was devised by Harrison, McNally, and Rowe³¹ for the determination of traces of fluorine and other non-metals in U_3O_8 with excellent sensitivity. A few other applications were attempted.

3.9 Qualitative-analysis Methods. A great many qualitative analyses have been performed by the standard method of volatilizing the sample in a graphite arc. It has frequently been necessary to look for the presence of a great many elements with maximum possible sensitivity and to report results that would be dependable to at least an order of magnitude in concentration. These analyses have often been a challenge to the analyst, since independent and sensitive physical tests have been available for corroboration in many cases. Niedrach³² has found that surprisingly good guesses at numerical figures for the concentrations can be made by comparison with a limited series of known mixtures. The effect on intensities of different matrices (volatile, refractory, etc.) and of different kinds of elements as major constituents can be judged by making up various combinations of known mixtures. Consequently, this effort is definitely worth while.

The copper-spark method has been used for the qualitative analysis of rare earths and for the analysis of very small samples. A weak spark exposure has been found useful for classifying different alloys, especially those of aluminum.

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Chapter 27

LOW-PRESSURE METHODS

By D. H. Templeton and J. I. Watters

Compared with gravimetric and volumetric methods low-pressure gasometric methods have the inherent advantage of extremely high sensitivity. These methods may be made very reliable by using specific properties of the gases to effect their separation. In recent years gasometric methods have advanced rapidly in importance for the determination of carbon, oxygen, nitrogen, and hydrogen in metals. This advance has resulted from the recognition of the influence even of low traces of these elements on the properties of metals. In the case of oxygen no comparable reliable method exists. Technical improvements in vacuum-line equipment and the use of induction heating have been material aids in the development of these techniques.

The possible sensitivity of the gasometric methods is apparent when it is considered that at room temperature 1 γ of carbon or 1.3 γ of oxygen as carbon dioxide (only half the oxygen in the carbon dioxide comes from the sample) in a volume of 100 ml exerts a pressure of about 0.015 mm Hg, and that pressures as low as 0.0001 mm Hg can be readily measured in this volume with a McLeod gauge. A greater limitation on the sensitivity is set by the magnitude of the blank values obtained, which may be of the order of 0.1 γ of carbon or oxygen even in the micro apparatus.

The low-pressure methods for determining carbon differ radically from the vacuum-fusion methods for other elements, including oxygen, hydrogen, and nitrogen. In the carbon determination the constituents of the sample react with oxygen upon being heated in a platinum crucible in an atmosphere of pure oxygen at reduced pressure. The process is accordingly called "low-pressure combustion." After the combustion has taken place, the oxides of carbon are separated from the oxygen and determined in various ways.

In the vacuum-fusion method for oxygen, nitrogen, and hydrogen certain constituents of the sample, on being fused, react with the carbon of the very hot graphite crucible under a high vacuum. Volatile products such as carbon monoxide, nitrogen, and hydrogen are separated from each other and determined by various methods. All weight calculations may be made on the basis of Boyle's law. With regard to oxygen and carbon the methods are of course complementary, inasmuch as oxygen is the reagent in the determination of carbon, and vice versa.

A third type of vacuum procedure, called the "vacuum-extraction method," consists in heating the sample in a vacuum until certain volatile constituents are removed.

These methods have been used rather extensively at the larger centers of the steel industry during the last twenty years, especially in England and Germany. An apparatus for the low-pressure determination of carbon has recently been described by Wooten and Guldner¹ and Yensen² and further refined by Murray and Ashley³ and Murray and Niedrach.⁴ Papers on the vacuum-fusion method for oxygen include the studies of Derge,^{5,6} Hoyt and Scheil,⁷ Sloman,^{8,9} Vacher and Jordan,¹⁰ and Thompson and Holm.¹¹ Various methods for oxygen are discussed by Thompson, Vacher, and Bright.¹²

In addition to the considerations of time and the cost of apparatus, the reluctance of analytical chemists to adopt vacuum-line procedures has been due partly to their lack of familiarity with the possibilities of high-vacuum techniques and partly to erroneous ideas about the extent of the adsorption by glass of gases at low pressures and about the difficulty of the transportation and manipulation of such gases. Prescott and Morrison¹³ have shown that microgram amounts of gases may be manipulated in glass systems with mercury cutoffs and Toepler pumps without noticeable losses. It is also well established that mercury-vapor pumps can be used to transfer and circulate microgram amounts of gases. The vacuum lines discussed in this chapter, with the exception of the quartz combustion chamber, can be constructed by anyone possessing moderate glass-blowing skill. The operations for routine determinations, particularly the carbon determination, can be learned by a capable technician in a few days.

Thompson and his coworkers^{14-25,30} directed their attention toward the determination of impurities in uranium such as oxygen and hydrogen, for which macro samples were available. Consequently, it was possible to employ macro apparatus similar to the device described by Vacher and Jordan,¹⁰ which was already in routine use.

1. PRINCIPLES OF THE METHODS

1.1 Carbon. The classical gravimetric procedure, described in the chapter on carbon, hydrogen, and oxygen, has been quite useful for samples containing milligram quantities of carbon. A conductivity method using a micro combustion train and a micro conductivity cell containing sodium or barium hydroxide to absorb the carbon dioxide was studied by Watters and Sheel.²⁹ Though very sensitive, this method was subject to the many mechanical difficulties involved in using a fine capillary tube to bubble the combustion gases through a small volume of alkali solution. Frequent clogging and breakage of the capillary occurred.

The low-pressure combustion method for carbon consists in burning the sample in an atmosphere of oxygen at reduced pressure, pumping off the combustion gases by means of a mercury-vapor pump, separating the carbon dioxide from the water by passing the gases through a trap at about -130°C , and measuring its pressure with a McLeod gauge.

Vacuum-line procedures for determining carbon and oxygen are more expensive than most classical chemical determinations because of the cost of special equipment, such as vacuum pumps and induction heaters. The low-pressure combustion method for determining carbon in most metals requires temperatures below 1600°C . Consequently, a relatively inexpensive arc-type induction heater of about 3 kw output will suffice for most determinations.

1.2 Oxygen. The classical methods for determining oxygen in metals are not specific. The various procedures consist in the solution or vaporization of the free metal by treatment with a reagent such as an acid or a free halogen, or by electrolysis, which leaves a residue that is assumed to be the oxide. Thus, uncombined oxygen in solution is entirely missed.¹⁰ Such methods are useful only for relatively pure samples in which chemically combined oxygen is the major nonmetallic impurity. In general, the sensitivity is limited to amounts of residue that can be weighed. The various methods are discussed by Thompson, Vacher, and Bright.¹² Orlemann and Hageman^{31,32} have investigated a bromine method in which the residue is measured by alpha counting. This procedure extends the theoretical sensitivity to the micro range, but a satisfactory procedure was not developed.

The vacuum-fusion method for oxygen consists in fusing the metal sample in a graphite crucible under vacuum and analyzing the evolved gases. The oxygen is evolved chiefly as carbon monoxide, together with a small amount of carbon dioxide. The carbon dioxide may be determined as described above for carbon. The carbon monoxide is

oxidized to carbon dioxide by circulating through hot copper oxide and is measured in the same way. Hydrogen and nitrogen in the evolved gases can also be determined. Alternate procedures for the gas analysis are discussed below.

As the vacuum-fusion methods for oxygen require higher temperatures, an oscillator of greater energy output and a quartz combustion chamber are required. The initial cost of the induction heater is high, and the upkeep of the vacuum-tube type, at least, is appreciable as a result of the necessity of replacing tubes. The cost and performance factors associated with the oscillator should improve as a result of the recent increase in their use. The vacuum-fusion procedure also requires considerable time and care. The determination of a single sample as a result of the recent increase in their use requires 5 or 6 hr.

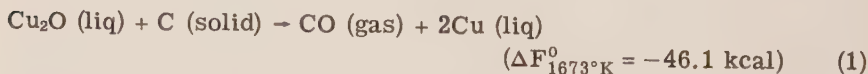
The vacuum-fusion procedure has not produced uniformly excellent results. Early workers obtained low results for oxygen in steel in the presence of silicon and manganese.¹⁰ Pieces of silicon dioxide appeared to float on the molten surface without reacting. Manganese deposited as a mirror on the upper portions of the chamber, where it combined with oxygen. The use of metal baths, higher temperatures, more rapid pumping, and frequent cleaning have minimized these difficulties.

The violence of the reaction with pure oxides limited their usefulness as standards. Inhomogeneity of ingots has been a disadvantage in their general usefulness as standards. Furthermore, micro samples may behave physically in a different manner from macro samples because of wetting and floating effects. The earlier workers²⁵ used an iron bath and kept the temperature in the range of 1600 to 1750°C. Above this temperature range the volatility of iron becomes excessive thus introducing a difficulty similar to the disturbance caused by manganese in steel. Later workers,²⁸ accordingly, dispensed with the iron bath and resorted to higher temperatures, reaching 2500°C for some substances. This very high temperature is difficult to attain and is accompanied by increased volatility. The pressure of demands for immediate analysis limited the opportunities for a systematic study on samples of greatly varied composition. However, the method appears to give accurate results in many cases.

The fundamental chemical reaction of the vacuum-fusion method for oxygen analysis is the reduction of a metal oxide by carbon. Generally, almost any metal oxide can be reduced by carbon if the temperature is high enough and the pressure is sufficiently low. It is necessary only for the equilibrium pressure of carbon monoxide to be greater than its partial pressure in the system. In practice the equilibrium pressure must be great enough to permit the reasonably

rapid evolution of gas. Another very important factor is the rate at which the material comes into contact with the carbon so that reaction becomes possible. The sample usually must be melted; hence the name "vacuum fusion."

The equilibrium pressure of carbon monoxide can be calculated from the free energies of formation of the metal oxide and the carbon monoxide. Thompson³³ has given such data as the functions of temperature for the oxides of 32 metals. As an example, the following calculation can be made from his data:



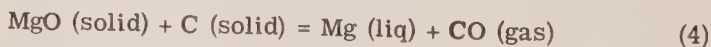
At equilibrium, ignoring solution effects,

$$-RT \ln K_p = -RT \ln p_{\text{CO}} = \Delta F^0 \quad (2)$$

$$p_{\text{CO}} (1673^\circ\text{K}) = 10^6 \text{ atm} \quad (3)$$

For cupric oxide the equilibrium pressure is even greater. Thus the oxygen should be completely removed from copper in the vacuum-fusion process. It has been found experimentally that at 1400°C 99 per cent of the gas is evolved in 1 to 3 min, which agrees with the expected pumping speed of the pumps used. It should be observed that a reduction may occur in vacuum even if the standard free energy for the reaction is several kilocalories positive because the equilibrium pressure need only exceed the pressure of the system.

This calculation assumes that no solutions or carbides are formed and that the oxide and metal remain in the crucible. Obviously, if the oxide is volatile, low results may be obtained. If the metal is volatile, the equilibrium pressure of carbon monoxide is even greater than the pressure calculated as in the above illustration. As an example, the equilibrium pressure of CO for the reaction



is calculated from Thompson's data³³ as 10^{-6} mm Hg at 1380°K, the boiling point of magnesium, in the presence of saturated magnesium vapor. But if magnesium is allowed to distil out of the crucible, reduction will occur if the pressure of the system is less than 0.05 mm Hg. A complication is introduced by the possible recombination of the metal and the carbon monoxide at lower temperatures outside the crucible, but good results are possible even when some distillation of

the metal takes place. Apparently, a periodic cleaning of the chamber is advisable, though not mandatory, between each pair of samples. If a solution is formed, the activities of the metal and the oxide will be decreased by amounts that cannot ordinarily be predicted from the available data. The activity of carbon at equilibrium will remain unchanged, since the crucible furnishes an excess and all phases become saturated with carbon. If a carbide is formed by the metal, the increase of free energy must be more negative, and the equilibrium pressure of the carbon monoxide must be greater. Thus, stable carbide formation is thermodynamically favorable to the vacuum-fusion process.

Reliable values are not available for the free energies of formation of uranium oxides and carbides at high temperatures. Brewer³⁴ has given estimates based on data for lower temperatures. Heusler³⁵ has made direct measurements of the equilibrium pressure of carbon monoxide with a mixture of uranium dioxide and graphite at high temperatures. This pressure increases rapidly with temperature, 1 atm at about 1800°C. However, Heusler did not determine unambiguously what solid phases were present in his experiments. The data from both these sources indicate that uranium oxides should be readily reduced with graphite if equilibrium can be attained at a reasonable rate.

The rate of reaction is more difficult to calculate, but fortunately at these high temperatures most reactions are sufficiently rapid if the reactants can come into contact. The substance is usually melted, but this is not always necessary. Uranium and thorium oxides, for example, can be completely reduced at temperatures far below their melting points.

The final test in any case must be experimental. If the conditions are suitable, most of the gas will come off in a moderately short length of time, and the rate of evolution will afterward approach the rate observed before the addition of the sample. Owing to the lack of reliable, independent methods of analysis, metal samples of known oxygen content for use as standards are not easy to obtain. However, if good results are obtained with pure oxide samples, which are frequently more difficult to reduce than a small amount of oxide in a metal sample, the results for the corresponding metal should be trustworthy.

Good results have been obtained with pure uranium oxides.²⁸ Much difficulty is reported in obtaining quantitative recovery from simulated uranium samples consisting of uranium oxide in the presence of uranium metal, especially at higher temperatures. When an iron bath is used, at 2000°C the reaction is so violent that the samples may be

lost. Uranium carbide formation may make the bath sluggish, and the results frequently seem to be a function of the temperature (see references 14, 16, 18, 19, 22, 24).

At the high temperatures used in the vacuum-fusion method nearly all the oxygen is evolved as carbon monoxide, which must be oxidized to carbon dioxide before it can be condensed by liquid nitrogen or absorbed by Ascarite or soda lime. The most convenient method of effecting the oxidation is to pass the gas through a tube containing cupric oxide at 300 to 400°C. The reaction is as follows:



From the data given by Thompson³³ the values of the equilibrium constant *K* in Table 27.1 can be calculated. The equilibrium is so far in

Table 27.1—Equilibrium Constants and Oxygen Vapor Pressures over Copper Oxide

Temperature, °C	$K = p_{\text{CO}_2} / p_{\text{CO}}$	p_{O_2} , mm Hg
300	2×10^{14}	6×10^{-12}
400	2×10^{12}	4×10^{-8}
500	6×10^{10}	2×10^{-5}
600	4×10^9	3×10^{-3}

the direction of carbon dioxide that quantitative conversion can be obtained at any of the temperatures given.

The vapor pressures of oxygen, according to the reaction



are also given in Table 27.1, as calculated from Thompson's data.³³ Thus at 500°C the pressure of oxygen becomes appreciable and may cause errors in the analysis. The rate of reaction for Eq. 5 increases with rising temperature, and, since it is only moderately rapid, the highest possible temperature is advantageous. For these reasons 300 to 400°C is usually chosen as the optimum temperature range of operation of the furnace.

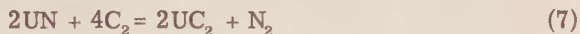
The rate of oxidation is also a function of the history of the copper oxide. Best results were obtained with cupric oxide wire that had been alternately reduced with hydrogen and oxidized with oxygen several times while being heated at 300°C. This operation need not be dangerous if the proper precautions are taken to remove each gas com-

pletely before the other is admitted, but carelessness may result in a serious accident.

After considerable use of the copper oxide the rate of oxidation becomes slower. Heating in pure oxygen usually restores the copper oxide to its original condition. If the furnace is left hot when air is admitted to the system during the sample-loading process, enough oxidation takes place so that other treatment is seldom necessary.

Fifteen to sixty minutes, depending on the condition of the copper oxide, has usually been the time necessary for the oxidation of the carbon monoxide from one sample.

1.3 Nitrogen. In the vacuum-fusion analysis of many metals, for example, iron, any nitrogen present in the sample is evolved as the gas. Nitrogen is measured with helium or any other inert gas as the residual gas which cannot be condensed with liquid nitrogen after passing over hot copper oxide. That metals of the actinide series form surprisingly stable compounds of the type MN is well known. It has been shown by Newton, Nottorf, and Doane³⁶ that, although higher nitrides are unstable, UN can be heated to 2300°C in vacuum without decomposition. Because of carbide formation the reaction



is more likely to proceed than the decomposition of UN into the elements. These authors reported that UN will react with graphite at 2250°C, but the reaction products have not been identified. However, Brewer²⁶ stated that uranium nitride is thermally unstable at 1800°C in the presence of carbon in a vacuum. This fact indicates that vacuum fusion can be used for the determination of nitrogen in uranium samples.

Several samples of uranium and thorium in which nitrogen had been determined by the Kjeldahl method were analyzed by the vacuum-fusion method at 1850°C without the iron bath. The resulting gases always contained but a small fraction of the amount of nitrogen reported on the basis of ammonia-distillation methods. The amounts found were of the order of magnitude of the blanks.

The use of an iron bath yielded consistent results for nitrogen, which tended to be somewhat lower than those obtained by the Kjeldahl method.^{14,22,25}

1.4 Hydrogen. Uranium hydride, UH_3 , is so unstable at high temperatures that any hydrogen present in a uranium sample will be evolved as the gas during vacuum fusion. The dissociation pressure of uranium hydride at 25°C, obtained by extrapolation from experimental data³⁸ for the range 250 to 440°C is 10^{-6} to 10^{-5} mm Hg. This

pressure is enough to cause complete decomposition during the long degassing period, unless the diffusion rate is too slow. The accuracy of the hydrogen determination is uncertain also because it is measured by a small decrease in a large volume of gases. Accordingly, as a check, Thompson and his coworkers²⁵ determined the hydrogen by a vacuum extraction in an apparatus essentially similar to the one described by Holm and Thompson.³⁷ The uranium was heated by induction in a silica crucible within a quartz furnace. At 800°C the extraction was complete in 1 hr. Below 800°C the extraction was too slow for practical use. The results according to the vacuum-fusion and the vacuum-extraction methods agreed very well, thus indicating that, at least for low hydrogen content, the vacuum-fusion method may be used.

2. METHODS OF GAS ANALYSIS

Liquid reagents used by the Orsat apparatus are not suitable for low-pressure analysis because of their relatively high vapor pressures. In one method, consequently, solid reagents are used, and the gases are transferred with a Toepler pump or a mercury-diffusion pump. The pressure and volume of the gas after each absorption are measured with a capillary pipet or McLeod gauge. First, water is absorbed in magnesium perchlorate. Carbon dioxide is absorbed in soda lime or in Ascarite with a little magnesium perchlorate at the ends of the packing to absorb the liberated water. If the hydrogen and carbon monoxide are in excess of the oxygen, the gas is passed over a hot platinum wire and the magnesium perchlorate in series to remove the oxygen and some hydrogen. Next, Ascarite¹⁰ or soda lime¹³ is used to remove any carbon dioxide formed in the previous step. The remaining hydrogen is removed by being passed through hot copper oxide and magnesium perchlorate in series. Carbon monoxide is also oxidized, but this action produces no change in volume. Finally, the gas is passed through the hot copper oxide and soda lime or Ascarite in series in order to remove the carbon dioxide. Nitrogen is left in the residual gas.

An alternative procedure makes use of fractional condensation in lieu of the chemical absorbers. On account of the great difference in magnitude of the vapor pressures of water, carbon dioxide, and permanent gases, as shown in Table 27.2,³⁹ clean quantitative separations can be made. A dry-ice trap at -78°C is inadequate for the quantitative condensation of water, but a trap at -100 to -130°C will remove it quantitatively without condensing any of the other gases. A liquid-nitrogen-cooled trap at -196°C will quantitatively remove carbon

dioxide from oxygen, nitrogen, and carbon monoxide. The -130 and -196°C traps can be substituted for the magnesium perchlorate and the soda lime, and the exact procedure outlined above, or various modified procedures, can be used. The cold traps offer much less resistance to the flow of the gases, and the difficulty of degassing the finely divided reagents is avoided. In addition, there is the important advantage that the traps can be warmed up and the gas can be recovered. Thus carbon dioxide is always measured directly instead of by difference. The direct measurement makes possible the determination of the very small quantity of carbon dioxide in the tremendous excess of oxygen in the carbon method. Water cannot be measured directly in a McLeod gauge because of its low vapor pressure and its marked tendency to adsorb on the glass walls.

Table 27.2—Vapor Pressure (mm Hg) of Various Gases

Temperature, $^{\circ}\text{C}$	H_2O	CO_2	O_2	CO	N_2
-78	6×10^{-4}	760			
-100	1×10^{-5}	104			
-130	6×10^{-9}	2.3	24,000		
-196	1×10^{-24}	9×10^{-9}	160	500	760

The measurement of the vapor-pressure curve for the material condensed in a trap makes possible the analysis of some mixtures that cannot be separated easily by the procedure outlined above. A modification of the procedures described by Sebastian and Howard⁴⁰ has proved useful. The trap is surrounded with a large split copper block machined to fit. A thermocouple is installed for temperature measurements. The trap and block are first cooled with liquid nitrogen in order to condense the gas sample. The permanent gases are then pumped out of the system. The liquid nitrogen is removed, and the pressure in the trap is measured at frequent intervals with a McLeod gauge as the temperature of the block slowly rises. The disadvantage of the condensation method lies in the expense of a constant supply of liquid air.

3. INDUCTION HEATING

Induction heating has been widely used in recent years in certain industrial applications for the rapid and controlled heating of metals.⁴¹⁻⁴⁴ The technique has been found very useful by chemists for heating objects in glass vacuum systems. Inasmuch as the method is

new and very little discussion of it can be found in the literature commonly available to chemists, some space will be devoted to it here. A more detailed mathematical treatment is given by Brewer.⁴⁵

When a body that is a conductor of electricity is placed in the field of a solenoid carrying an alternating current, an electromotive force is induced in that body. This action results in eddy currents, which dissipate as heat part of the electrical energy fed into the solenoid. Intervening walls of poorly conducting materials, such as glass, quartz, and water, have little effect. Thus it is possible to heat an object inside a glass vacuum system to a high temperature, while the walls of the chamber are cooled with water, without any mechanical connection between the object and the external electrical circuit.

For the transfer of sufficient energy the frequency of the alternating current must be of the order of 10 to 1,000 kc. Commercial spark converters are available which produce frequencies of 30 to 50 kc, as well as electron-tube oscillators that operate at about 500 kc. For laboratory use in heating small objects a power output of 5 kw is sufficient. The spark converters are much simpler and considerably cheaper, but their power output is rather variable. They are less suitable for experiments in which the heated object must be maintained at a closely regulated temperature. Unless the complete high-frequency circuit, including the heating coil, is shielded electrically, the damped oscillation produced by the spark and the tuned circuit may cause serious interference with neighboring electronic equipment, such as particle counters and radios. The electronic oscillators can be controlled much more precisely, and radiation from the sharply tuned, steady high-frequency current does not interfere with other electrical equipment.

It is possible, with a fairly simple approximate mathematical calculation, to determine the power consumed and the temperature attained by the heated object.⁴⁵⁻⁴⁹ The equations give considerable information about the effect of certain variables on the maximum temperature and make possible the intelligent design of crucibles.

The power dissipated in the object is a function of the intensity and frequency of the electromagnetic field and of the size, shape, and material of the object. The temperature attainable depends on this power and on the mechanism of heat transfer from the object to its surroundings.

The simplest case to treat mathematically, and one that is frequently used, is a cylinder coaxial with the heating coil. The induced currents travel in circles in planes perpendicular to the axis. At these high frequencies the "skin effect" becomes important; the cur-

rent density is much greater near the surface than in the interior of the body. This phenomenon may be explained by considering the shielding effect of the current at the surface. Its field inside the cylinder opposes the field produced by the heating coil, and the net field is smaller, thereby causing smaller currents. At high enough frequencies so much of the current is concentrated near the outer surface that the center of the cylinder can be removed without any appreciable effect on the energy received. The heat lost from such a shell is approximately the same as the heat from a similar cylinder, so that the temperature attained is nearly as great.

The effect of the size and dimensions of the heated object on the temperature attainable can be shown from equations for induction heating. The temperature increases as the height is increased, but when the height is much greater than the diameter, the effect is small. A height twice as great as the diameter is 80 per cent as effective as infinite height. For small diameters the temperature increases as the diameter increases. Very small objects are not heated to an appreciable extent.

The most important factor is the intensity of the field. The current is limited by the power source. For the General Electric 5-kw oscillator the maximum value is 120 amp. The turn density is limited by the size of the conductor, usually a copper tube through which cooling water is flowing; it must be large enough ($\frac{1}{8}$ to $\frac{1}{4}$ in. in diameter) to carry the current without prohibitive heating. The turn density is also limited by the permissible inductance of the coil and the necessary length, which should be at least as great as its diameter and at least twice as great as the height of the cylinder heated. The inductance must be such as to tune the oscillator at the proper frequency. The diameter of the coil is important in that the inductance per turn is less for smaller diameters, thus allowing a larger number of turns for a given inductance. For small diameters the decrease in field due to the end effect is smaller. Another advantage of a small diameter is the fact that the external field is smaller, with less power dissipation in neighboring metal objects.

In class I heating⁴⁵ (the desired type) resistance is small, as compared with inductive reactance. The minimum diameter for efficient class I heating of an Acheson graphite crucible, using Brewer's value of 5.6×10^{-4} for specific resistance of graphite at 2200°C , is 4.1 cm for 30 kc and 1.0 cm for 500 kc. As the crucible is made larger, it dissipates more power, decreases the magnetic field, and increases the apparent resistance of the heating coil. This procedure decreases the heating and, in the case of the spark converters, greatly increases

the degree of damping of the high-frequency oscillation. The crucible should be made large enough for class I heating, but not much larger, if the highest possible temperature is desired.

For an object not of cylindrical shape the amount of heating is of the same order of magnitude as is obtained with the largest cylinder, or cylindrical shell, that can be cut from the object. A thin-walled cylindrical shell that is ordinarily heated to a considerable extent will, if it is cut completely through at one point in a vertical direction, be heated only negligibly. As the ratio of surface to diameter is increased, the temperature attained with a given power input is decreased because of greater radiation.

At low temperatures less heat is lost through a vacuum than through an insulating solid, but at high temperatures radiation losses increase very rapidly with increasing temperatures. The use of insulating materials introduces experimental difficulties. For example, in the vacuum-fusion method for oxygen analysis any gas adsorbed on the insulation is slowly removed during heating. The rate at which it is evolved determines the lower limit of detection of gas from the sample. Brewer used a graphite crucible insulated with powdered graphite (not greatly heated),⁴⁵ as well as graphite crucibles insulated with Carbocell 60, a porous form of carbon with high electrical resistance, and supported in a vacuum.²⁶ With a General Electric 5-kw 500-kc oscillator the temperature can be raised to 2400°C, several hundred degrees higher than can be obtained with a simple crucible. The crucible²⁸ is surrounded by three concentric cylinders of Acheson graphite and is covered with a funnel. The shields and funnel are cut in many places, and a few ribs separate the parts, so that much of the heating is concentrated in the crucible. The various pieces are staggered in order to leave no cracks for radiation from the center except through the hole in the top.

Another method of decreasing the heat lost by radiation is to silver the inside of the chamber so that some of the radiation will be returned to the crucible. A mathematical consideration of this situation will reveal that, unless the chamber is almost completely silvered (including the top and bottom), the increase in temperature will be very small.⁴⁵ If the silver film is unbroken, it too will be heated by the induction. The heating may make pieces come loose from the walls. At high temperatures many materials are distilled from the crucible and deposited on the walls, thus destroying the effect of the mirror. Because of the many difficulties encountered this method has not received much application.

3.1 Apparatus. (a) Special Materials and Equipment.^{27, 28} Pyrex glass has been found satisfactory for the various combustion cham-

bers used with the carbon apparatus, in which a platinum crucible is heated to 1000 to 1400°C. No breakage has ever been caused by thermal shock, even though in some chambers the clearance between the walls and the crucible is only a few millimeters. The chambers are always water-cooled on the outside.

In the oxygen apparatus, in which much higher temperatures are required, fused quartz has always been used for the chamber. Difficulty with pyrex due to breakage has been reported. Quartz is also used for the catalyst tube in the carbon apparatus for burning the impurities in the oxygen. The good quality of commercially available graded seals eliminates any difficulty in joining the quartz parts to the rest of the pyrex vacuum system.

It is routine practice with the carbon apparatus to crack open the pyrex combustion chamber whenever cleaning is necessary and to seal it together again with a hand torch. The chambers can survive a dozen or more such operations. In the top of the quartz chamber of the oxygen apparatus is incorporated a standard-taper (34/45) ground joint²⁸ to facilitate its opening. This joint is sealed by spreading Apiezon W cement on the male part and inserting it in the female part, heating both parts gently in the meantime with a hand torch. The joint can be opened easily when it is heated with a torch if care is taken during the sealing operation not to make the film of wax too thin.

Apiezon N stopcock grease has been in general use for all stopcocks and other ground joints. Many other good vacuum greases are on the market, but it should be mentioned that the common grease sold for burets is not satisfactory for high-vacuum use.

Pyrex Dewar flasks are somewhat more expensive than soft-glass flasks, but the extra cost is more than compensated for by their longer life and added safety, particularly when liquid nitrogen is used. A very valuable safety practice is to pack the flask with asbestos fiber in a galvanized sheet-iron can of the same height but of half an inch larger diameter. When such a flask is broken, nearly all the glass and contents will remain in the can, with little danger of injury to personnel or equipment.

A number of types of commercial and shop-made mercury diffusion pumps have been used on the apparatus. The only pumps whose performance is very critical are those used for pumping the gases into the measuring volume of the oxygen apparatus. The pump must sometimes operate against a considerable backing pressure, and its effective volume from the orifice to the high-pressure outlet must, since it is part of the measuring volume, be constant if good results for hydrogen or nitrogen are to be obtained. The accuracy of the oxygen measurement does not depend on this pump. The Princeton type

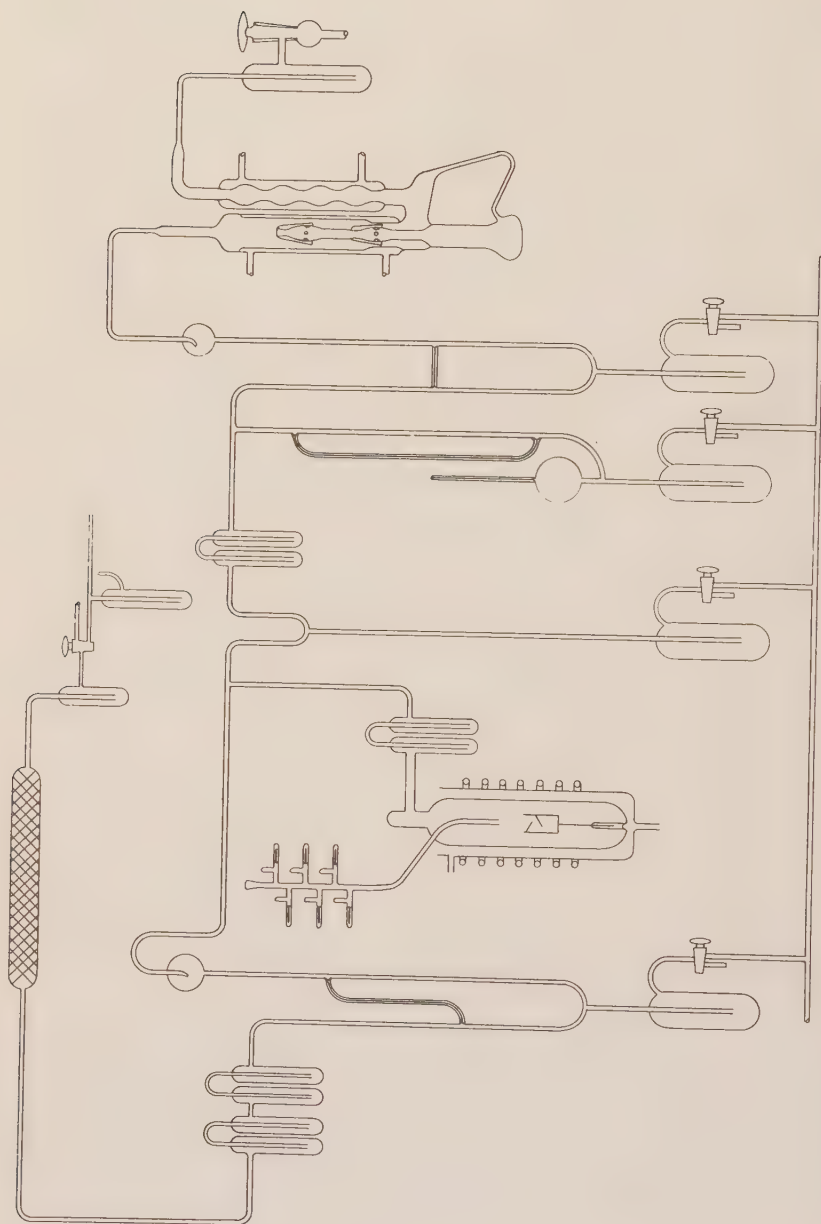


Fig. 27.1 — Micro low-pressure apparatus for determination of carbon.

of pump, if operated at a fairly high rate of mercury flow, is quite satisfactory, but a small single-stage pump is probably better. For other purposes the performance of the Princeton type of pump has been uniformly good. The Brewer type of pump (made by Eck & Krebs) has a high pumping speed, but owing to its small cooling surface it has a tendency to distil mercury into other parts of the apparatus, unless the exit tube is fitted to a condenser.

A potentiometer and thermocouples are necessary for regulation of the petroleum-ether bath in the condensation procedures and for many special experiments, such as determinations of vapor-pressure curves. An optical pyrometer is essential for the operation of the oxygen apparatus and is useful for the carbon procedure.

The water trap is cooled by a bath of petroleum ether at about 130°C. At first, more complicated arrangements were used, but it was finally found that a quart Dewar flask of petroleum ether could be kept sufficiently cold by intermittent stirring and the occasional addition of liquid nitrogen. (Do not use liquid air!)

(b) Carbon Apparatus. The micro low-pressure carbon apparatus was based fundamentally on the macro apparatus of Wooten and Guldner¹ and Murray and Ashley.³ The experience of Prescott and Morrison¹³ was useful in avoiding too small a tubing. The unit, which gave remarkably trouble-free service, is shown in Fig. 27.1. Details are reported by Templeton, Niedrach, Byerly, and Watters.²⁷

(c) Vacuum-fusion Apparatus. The vacuum-fusion equipment has been so varied in design that a discussion of the apparatus is given in the collected papers by various authors for which references have already been given.

4. ANALYSIS OF VARIOUS TYPES OF SAMPLES

Uranium, like many other metals, tarnishes rapidly in air until it is coated with a dark oxide layer. In order to avoid error from this source the samples are carefully cleaned with nitric acid, washed with acetone and ether, evacuated in glass ampoules, and sealed under vacuum. This treatment leaves the surface bright and in such a condition that brief exposure to air for purposes of weighing and placing in the apparatus introduces negligible contamination by oxygen. Thorium and beryllium samples are cleaned mechanically by scraping or filing. Some samples have been analyzed without cleaning because total oxygen, including surface contamination, was desired. No practical method exists for cleaning powdered samples.

Samples are most conveniently handled as single pieces. Powders may be wrapped in gold foil, but this technique is more difficult, and

the oxygen contained in or adsorbed on the gold considerably decreases the sensitivity of the method. In practice the latter objection has not been serious because powdered samples are usually oxides containing rather large amounts of oxygen. Similar empty pieces of gold foil are analyzed to obtain a correction for their oxygen content.

In determining suitable conditions for analyzing new types of samples, one procedure has been to analyze several portions at successively higher temperatures from about 1200 to 2200°C. The blanks, which increase with temperature, become large at higher temperatures. The pressure is read on the gauge at 2-min intervals, and pressure-time curves are plotted. The optimum temperature is that at which the gas is evolved at a sufficiently rapid rate to keep the total blank at a minimum.

Many short cuts are possible after the analysis of a given type of sample has become routine. The gases evolved by a given type of sample at a fixed temperature frequently contain a constant percentage of carbon monoxide and carbon dioxide. At high temperatures less than 1 per cent of the oxygen is evolved as carbon dioxide. If little hydrogen and nitrogen are evolved, it may be satisfactory to measure only the total pressure of the evolved gas. In other cases the determination of carbon dioxide before converting the carbon monoxide can be omitted.

Time-pressure graphs are valuable for establishing the minimum length of time necessary for the various pumping operations. The condition of the copper oxide tube (for the ignition of CO) should also be checked periodically by this method. The conversion can be readily followed during any procedure because the carbon dioxide is removed as it forms.

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Chapter 28

RADIOCHEMICAL ANALYTICAL METHODS

By G. E. Boyd and D. N. Hume

Recent advances in the study of nuclear phenomena have made it appear that radioactivity is a universal property of matter. Today each of the 96 elements is known to possess at least one radioactive isotope. Furthermore, the ratio of active to stable nuclear types throughout the periodic table is now roughly two to one. Some inkling of the magnitude of the development that has taken place may be obtained by noting that since the discovery of artificial radioactivity in 1933 over 445 new isotopes have been described, thus raising the sum total of active nuclear species, artificial as well as natural, to at least 490. Together with this quantitative increase in our knowledge of the diversity of nuclear types and properties, a corresponding development has taken place in the instruments of nuclear science, both for the production and for the detection and measurement of radioactivity, as illustrated by the cyclotron, the linear accelerator, the betatron, and the chain-reacting pile, to name but a few, as well as the alpha pulse-counting chamber, the Geiger-Mueller tube, and the ionization chamber with its attendant electronic high-voltage supply, amplifiers, scaling circuits, and recorders. Such advances as these will certainly exert a profound influence upon the development of inorganic chemistry in the near future, and they will have considerable effect upon the oldest branch of this subject, namely, inorganic analysis.

Radioactivity seems likely to prove of importance to analytical chemistry in several ways. A number of purely instrumental methods of analysis will surely be developed as by-products of research in nuclear science. For example, extremely small quantities of an element may be detected by virtue of the ionizing properties of the radiations emitted by its radioisotopes. Instruments already available permit the rapid and accurate measurement of these minute quanti-

ties with very great convenience and with a large resultant economy of time in the conduct of routine operations. An additional and distinctive advantage of radioactivity for use in analysis is its freedom from interference in detection. In all but quite exceptional instances neither the decay nor the radiation characteristics of an active isotopic species are affected by environment. Consequently the rapid estimation of elements with enormous sensitivity is possible directly and without chemical separation, and great simplifications in chemical analytical problems in plant production work may be expected. Very often it is necessary to hold up a process until time-consuming chemical analyses have been made by the control laboratory. If a tracer is introduced at the beginning of the process, it is possible to achieve a simple, quick, and often automatic analysis by radioactive measurement that will eliminate the usual holdup. The patented use of radiophosphorus to follow phosphorus in steel refining serves as an illustration.

In the future a second application of nucleonics may come through the development of the activation method of analysis. In this procedure use is made of nuclear transformation reactions, induced either by energetic charged particles or by neutrons, which give rise to active nuclei. These artificial activities may then be detected and measured either with or without previous chemical separation, and the radioactivity observed may be used to estimate the amounts of parent nuclei. In certain instances this method is capable of far exceeding the sensitivity of spectroscopic analytical procedures in the detection of trace impurities.

In the third place, radioactive isotopes will certainly be utilized extensively for many purposes both in applied analysis of the more conventional type and in research. In this connection the use of radioactivity falls into two categories: (1) the employment of the energetic and very penetrating radiations emitted by radioactive elements and (2) the use of the property of radioactivity as a tag for the atom possessing it (the method of radioactive indicators). Thus, when an active isotope of an element is used in the presence of common, inactive isotopes (i.e., "carriers"), it may serve to "indicate" the path of the stable isotopes throughout the various chemical or physical changes that they may undergo. If the ratio of the amount of the active isotope to stable isotopes remains constant during all the phases involved, no information other than the course of the element is revealed. However, this ratio is frequently altered owing to a distribution of activity between two sources of inactive isotope, and some type of exchange process of analytical significance may thereby be

disclosed. Hence, through the simple expedient of "labeling" or "tagging" some of the atoms in a mixture it becomes possible to study many problems basic to inorganic analysis.

Since at any given time the amount of alpha, beta, or gamma activity exhibited by a radioactive substance is directly proportional to the masses and to the relative abundances of the active isotopes that the substance contains, radiometric methods are rendered possible. These procedures are frequently of paramount importance in the quantitative estimation of the heavy elements (of atomic number above 83), and sometimes they are the only methods known, as, for example, in the determination of polonium, astatine, francium, and actinium. During the past several years the radioactive properties of both Pu^{239} and the uranium isotopes were, of course, used extensively for the analytical determination of the masses of these elements at various points in their respective separation processes.

Finally, another very important type of radiochemical analysis, known as "activity analysis,"⁴⁴ has come into being recently owing to the necessity for a quantitative determination of the radioactivity due to a given element in a complex mixture of radioactive elements, as, for example, the fission products of U^{235} . The results of activity analyses may be expressed either as absolute activity or in terms of the percentage of the total mixed activities due to the element in question. Since it will not be possible to devote space in this chapter to an exposition of the procedures followed in an activity analysis, a very brief description of the method will be supplied.

In analyzing the amounts of a radioelement that are produced in samples irradiated in the pile or at the cyclotron, it is usually inconvenient, even if feasible, to attempt to isolate quantitatively the submicroscopic traces therein. A carrier technique is generally employed. A predetermined mass of the desired element is added to a sample as an inactive carrier. The element is then separated from the mixture and purified by means of classical chemical methods. The active atoms accompany the inactive atoms, and the activity in the final precipitate is determined. The weight of the carrier recovered is measured, and the chemical yield of the fraction of atoms, both active and inactive, recovered in the chemical manipulations is then used to correct the observed activity of the final precipitate to 100 per cent recovery.

The following rutheruthenium determination affords a typical example: A solution of mixed fission-product activity was observed to have a total beta activity of 453,600 counts per minute per milliliter. To 1.00 ml of sample was added 20.0 mg of ruthenium as the chloride, and by appropriate chemical manipulations the ruthenium was isolated

and purified. The final precipitate of metallic ruthenium weighed 18.0 mg and gave a beta activity of 4,950 counts per minute. The chemical yield was therefore 90 per cent, and the count, corrected for chemical yield, was 5,500 counts per minute per milliliter, or 1.20 per cent of the total beta activity.

Only a few of the representative techniques and methods of applied radiochemistry will be described. An abbreviated treatment of the preparation of radioisotopes will then be presented, followed by a discussion of a few representative examples of the many recent applications of these radioisotopes to problems in inorganic analytical research. Next, a section will be devoted to the new and potentially highly useful activation method of analysis. Finally, some space will be given to a moderately detailed description of a number of important radiometric analytical methods used in the various uranium war-time projects.

1. METHODS AND TECHNIQUES IN APPLIED RADIOCHEMISTRY

1.1 Laboratory Practice in Determination of Alpha, Beta, and Gamma Radiations. (a) Principles. Radioactivity is detected and determined by means of the ionization caused by the charged particles emitted in radioactive decay. The passage of a charged particle through matter results in the formation of ions through inelastic collision. Since many ion pairs may be formed by the passage of a single charged particle, the detection of a single charged particle is often possible with relatively simple apparatus. Two fundamentally different approaches are employed in the determination of radioactivity. In one approach an effect proportional to the total ionization is measured, which gives the integrated effect of many particles. This is the principle involved in the use of the electroscope and the electrometer. In the other approach the effects of the bursts of ionization due to single particles are detected, as in the Geiger tube, pulse ionization chamber, or cloud chamber and in photographic track and scintillation methods. The method chosen to measure the ionization depends upon the type of radiation involved and upon its intensity.

Alpha radiation, which consists of charged helium nuclei emitted during radioactive disintegration, is characterized by short-range (several centimeters in air) highly ionizing particles. Several thousand ion pairs are produced in each millimeter of air through which a typical alpha particle has passed. This amount is much greater than for an average beta particle (a high-speed electron emitted in decay) or for a gamma ray (an electromagnetic radiation analogous in properties to an X ray), which produce 5 to 25 pairs and less than 1 pair per millimeter, respectively. By appropriate means the ioni-

zation due to each type of ray in a mixture may be detected and determined separately.

(b) Alpha-activity Measurements. Alpha activity is conveniently determined by means of the pulse ionization chamber, which consists of a pair of horizontal plates about 8 mm apart, with a potential of

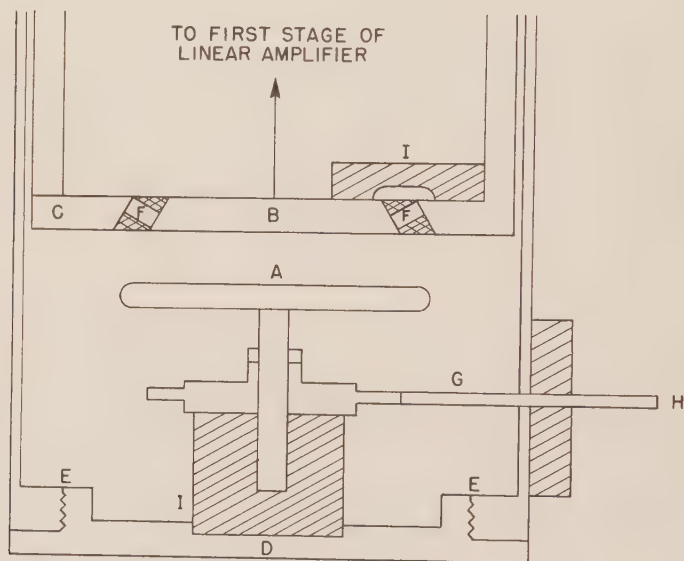


Fig. 28.1—High-geometry alpha-counting chamber. A, high-voltage electrode; B, collecting electrode; C, guard ring; D, bottom plate; E, breech thread; F, paraffin insulation; G, high-voltage wiping contact; H, high-voltage inlet; I, Amphenol insulator.

about 1,000 volts across the gap (see Fig. 28.1). The sample is placed on the lower electrode A, and the ions formed by the alpha particles are swept onto the electrodes by the electric field, thus causing a fluctuation in the voltage. This voltage pulse, which is of the order of 100 to 200 μ v, is amplified electronically to the order of volts necessary for easy detection. Since the pulse frequency is often too rapid to be handled by an ordinary mechanical recorder, an electronic device called a "scaling circuit" is used to eliminate all but a known fraction of the pulse to reduce the pulse frequency to a convenient magnitude. The characteristics of the counting system are so arranged that the smaller pulses due to beta and gamma rays do not trip the circuit, alpha rays alone being recorded.¹⁻⁵ A diagrammatic sketch of a complete system for counting alpha particles is shown in

Fig. 28.2. In the ordinary, "standard" alpha chamber the efficiency of detection is very close to 50 per cent, which is somewhat modified by back-scattering. Highly active samples may exceed the capacity of the instrument (about 30,000 counts per minute). A lower efficiency is obtained by use of a low-geometry counter, either the air-screen type, in which the lower electrode is a wire screen and the sample is is

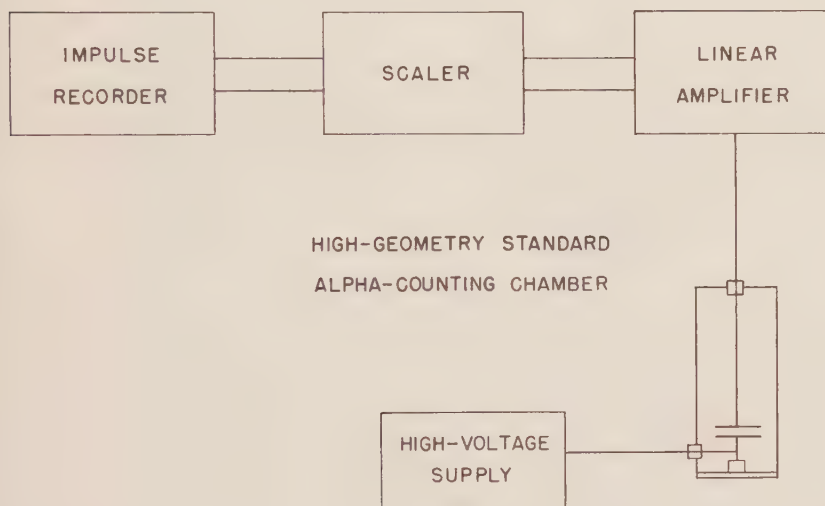


Fig. 28.2—Block diagram showing circuit components for the determination of alpha activity.

placed beneath it to yield an efficiency or "geometry" of about 10 per cent, or the vacuum type, in which the sample is at a considerable distance from the chamber, with the particles traveling in vacuum to the chamber and entering through a thin mica window. With the latter arrangement the geometry can be made very low without serious loss of accuracy. The method of detecting alpha disintegrations by visual observation of scintillations on a zinc sulfide screen is of historical interest only.

(c) Beta-activity Measurements. The measurement of beta activity is usually accomplished by using either an electroscope or a Geiger-Mueller counter.⁶ The Lauritsen quartz-fiber electroscope consists of a flexible quartz fiber fixed at one end and extending parallel to a stiff quartz rod. The quartz parts are sputtered with gold to make them conductive and are carefully insulated from the rest of the apparatus. The whole device is protected with an aluminum shield that



Fig. 28.3 — View of mica end-window type of Geiger-Mueller counter used in the Plutonium Project. (Photograph by courtesy of C. J. Borkowski and A. A. Jarrett, Clinton Laboratories, May, 1946.)

also acts as an ionization chamber and shuts out alpha radiation. The gold-covered quartz system is charged with 100 to 200 volts from a suitable source. This action causes the fiber to bend away from the rod because of electrostatic repulsion. Radiation passing through the instrument causes ionization of the air in the chamber, and the charge leaks away. This leakage results in a movement of the fiber that is observed through a microscope. The time necessary for the fiber to move through a standard distance gives a measure of the radioactivity of the sample. The activity is inversely proportional to time over a rather large range. The instrument is surprisingly sensitive and accurate, but its use with low activities is very tedious. For the measurement of soft beta and gamma radiation the electroscope has a high efficiency and is sometimes superior to the more elegant Geiger-Mueller counter.

The Geiger-Mueller counter, which is doubtless the most convenient method of measuring beta activity, has enjoyed very extensive use. The Geiger counting tube consists essentially of two electrodes, one usually a fine wire and the other a concentric metal cylinder about an inch in diameter. The space between the electrodes is filled with a suitable gaseous mixture (usually argon and ethyl alcohol) at a few centimeters pressure, and a potential of about 1,000 volts is applied across the electrodes. The voltage and the gas pressure are so adjusted that in the absence of ions in the gas no discharge takes place. A beta particle passing through the tube and producing one or more ion pairs initiates a cascade of ionization. A comparatively large surge of current results. The electronic "quenching" circuit to which the tube is attached is designed so that after a very short period of current flow (about 10^{-4} to 10^{-5} sec) the current is interrupted and the tube is recharged to enable it to detect another particle. The pulse is amplified and scaled down by a scaling circuit to allow high counting rates to be handled by a mechanical recorder. Suitable circuits and apparatus have been described (see references 1, 2, 7-11).

Geiger tubes are made in a variety of forms. The two most common types are the bell-shaped thin-windowed tube (see Fig. 28.3), which is desirable if soft radiations are to be studied but which requires a relatively constant and not too high room temperature for proper operation, and the traditional glass-enclosed type. The latter is more rugged and, though less sensitive to soft radiations than the thin-window type, is probably more satisfactory for general analytical work.

Beta activity may also be measured by an electronic circuit in which the current produced in an ionization chamber is measured.

Figure 28.4 shows the design of one such chamber. This apparatus, frequently called the "FP54" after the electrometer tube used in the amplifier, is used principally for high-activity measurement. The photographic darkening technique is used for certain special applications.

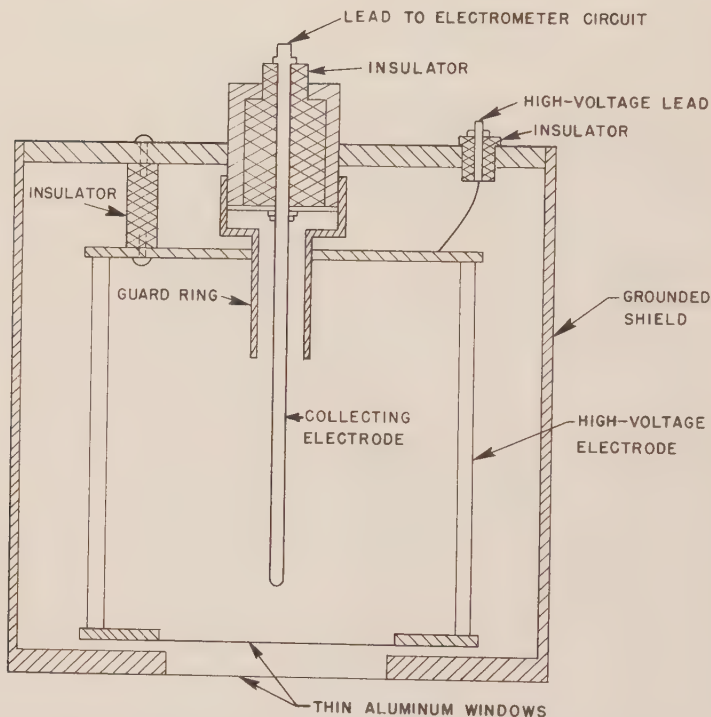


Fig. 28.4 — Ionization chamber for the measurement of beta-emitting radioactive samples.

(d) Gamma-activity Measurements. Since gamma rays are not charged particles, they are not detectable directly by ordinary counting devices. Instead, electrons ejected from matter by the passage of highly penetrating gamma rays can cause ionization, which is then detected. The ordinary Geiger tube may be used to detect gamma radiation in the presence of beta activity if a suitable absorber, such as a metal plate, is interposed between the tube and the sample to filter out all beta particles.¹²⁻¹⁴ The intensity of the gamma radiation is but slightly diminished, and the electrons ejected from the absorber and the tube walls are counted, the value given being proportional to

the gamma activity. Ionization chambers, particularly when filled with gas under pressure, are also used for determining gamma activity.^{15,16}

(e) Counting Techniques. Most experiments with radioactive indicators involve the comparison of a control sample with an unknown. In order to obtain reliable comparisons, care must be exercised to duplicate the conditions of measurement. Preparation of samples for counting usually involves their being mounted on a suitable medium or holder. For an alpha assay with the standard apparatus the active samples are usually evaporated on small platinum disks 0.5 to 1.0 in. in diameter. Small dishes may be prepared by raising the edges of the disks about 0.5 mm. These are useful for larger samples. Other containers, such as watch glasses and lusteroid cups, are less desirable. Alpha counting is usually done with a minimum of solid matter present in order to avoid absorption errors (see below). Small amounts of relatively dilute solutions are used for the evaporation. The mounted sample is placed on the lower electrode of the standard alpha chamber for counting.^{2,4}

Accurate beta and gamma counting requires that the sample be mounted in some reproducible manner with respect to the Geiger tube or whatever device is being used. This mounting is usually accomplished by attaching to the tube a standard aluminum frame of "shelves," consisting of slots to hold 3¼- by 2½-in. cards, on which the activity is mounted. Figure 28.5 serves to illustrate the mounting of the Geiger-Mueller tube in its lead shield together with the shelves in their working positions. The actual sample is usually placed on a 1-in. watch glass attached to the middle of the card.^{2,12} Figure 28.6 shows the details of this sample-mounting technique. Since beta and gamma radiations are more penetrating than alpha radiation, it is possible to mount solid samples and also to cover the active material without serious loss of sensitivity. Liquid samples may be counted directly for gamma activity with a high-pressure ionization chamber.¹⁶

A number of factors involved in mounting may have a significant effect on the observed counting rate. A fairly obvious factor is the geometry, which is the effective solid angle of the sample subtended by the sensitive part of the counting device. For a given instrument this angle is fixed by the placement of the shelves for holding the mounted samples. Another factor is absorption, the process by which radiation is stopped by matter before it enters the counter. This factor is very important in alpha counting, since the rays can be stopped completely by relatively small amounts of matter. The effect may also be important in beta counting but is generally of no significance in gamma counting. "Self-absorption" is the term ap-

plied when the absorption takes place within the solid or liquid sample emitting radioactivity. In alpha measurements such self-absorption may be very serious. For the determination of polonium alphas, in which the sample is mounted on a 1-cm square plate with various weights of solid matter, the loss would be about 1 per cent for 0.2 mg,

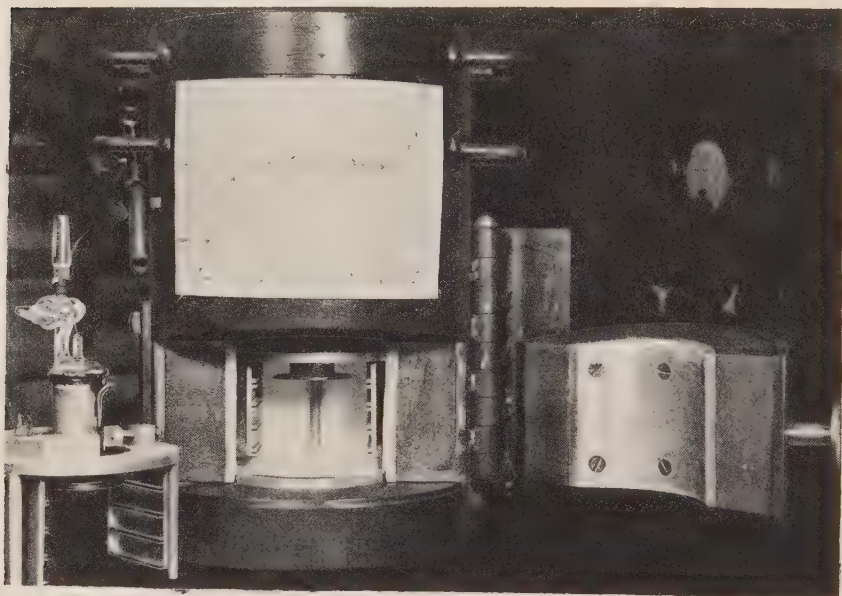


Fig. 28.5—View of Geiger-Mueller counter in its cylindrical lead shield, together with the standard shelf frame for positioning active samples. (Photograph by courtesy of C. J. Borkowski and A. A. Jarrett, Clinton Laboratories, May, 1946.)

5 per cent for 1 mg, 50 per cent for 10 mg, and 90 per cent for 50 mg. Self-absorption is less conspicuous with beta particles of ordinary energies (about 1 per cent for 10 mg), but with very soft beta radiation the loss may be high.

Scattering phenomena, in which particles not initially directed toward the counting device are directed toward it by interaction with surrounding matter, tend to counteract absorption to a greater or lesser extent. Scattering due to substances on which the sample is mounted is known as "back-scattering" and is quite appreciable for both alpha and beta activities. Self-scattering due to the particles of radioactive substances may itself be very high for some beta emitters, the counting rate being increased as much as 30 per cent. It

is very difficult to eliminate scattering, but by the use of carefully standardized mounting conditions the scattering errors can frequently be made uniform.¹²

(f) Calculation of Results from Measurements of Radioactivity. The calculation of the absolute disintegration rate from counting data

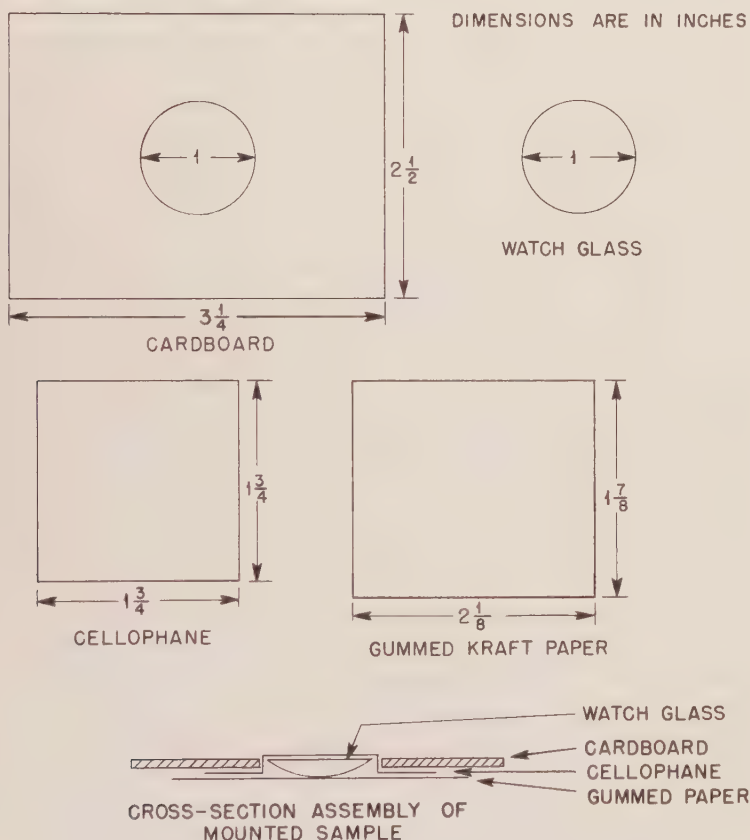


Fig. 28.6 — Sample-mounting technique.

involves a multitude of conversions and corrections. For ordinary analytical work it is seldom necessary to go to this trouble. A comparison of relative counting rates taken under the same conditions of geometry, absorption, and scattering is adequate for almost every purpose. A number of corrections must be made, however, before raw data can be applied to calculations. The data obtained from a counter is in terms of the total number of counts per minute. If the counting

rate is greater than a few hundred counts per minute, it must be corrected for coincidence losses (empirical coincidence corrections are usually available). The background (the number of counts, or scale divisions, or other units of measure that are recorded in the same time interval with no active sample present) must be subtracted from the observed value. This correction is true of electroscopes and ionization chambers as well as of counters. Finally, the efficiency of the instrument varies from day to day and possibly from hour to hour; accordingly, it must be checked by counting a standard sample of essentially constant activity. Alpha-counting rates obtained at different geometries may be compared with relatively little difficulty. This comparison cannot be made with beta- or gamma-counting rates unless special calibrations have been carried out for the activity being used.

If the activity under study decays at an appreciable rate or if a significant amount of daughter growth occurs, appropriate corrections must be made in accordance with the law of radioactive decay.^{17,18} As a matter of convenience, all counting rates are corrected for growth or decay to some arbitrary time, for which convenient graphical methods are available.^{12,19} Radioactive decay obeys the laws of probability, and at low counting rates statistical fluctuations are easily observed. The uncertainty in a counting rate is inversely proportional to the total number of counts recorded, so that, with low counting rates, long counts must be taken if accuracy is to be achieved. A statistical treatment of counting errors is discussed in reference 2. A rule of thumb is to take about 5,000 counts to obtain a probable error of 1 to 2 per cent. The probable error of a count is approximately equal to the square root of the number of counts recorded.

1.2 Preparation of Radioisotopes. As a consequence of the invention and operation of the chain-reacting pile, the availability of radioactive isotopes has increased enormously. The pile is now the major source of tracer material although the cyclotron will continue to be a very useful preparative instrument, as will, to a lesser extent, the other variety of charged-particle accelerators now known.

Still another and very fertile source of radioactive isotopes is uranium that has been made to undergo fission as a result of neutron bombardment. Radioactive species ranging from zinc (atomic number 30) through europium (atomic number 63), inclusive, have been isolated, and at present more than 150 active isotopes are known. This number is certain to increase, both because of more detailed investigations and because of the use of other fissionable elements. Also, as in the past, naturally occurring radioactive elements will continue as

sources of isotopes of elements beyond mercury (e.g., elements of atomic number greater than 80).

Thus, since the procurement of ample amounts of a desired radioactivity is no longer a major problem, it is well to examine the present status somewhat more closely. From a practical point of view certain limitations govern the use of radioisotopes in the field of inorganic analysis. First there are those considerations that deal with the radioactive characteristics themselves:

1. In general, the half life of the isotope is of prime importance, since it must be sufficiently long for convenient manipulation; otherwise, not enough activity will be available at the end of a series of chemical operations for accurate measurement. An example may be found in the element bromine, for which some seven radioactive isotopes are known, with half lives varying from less than 1 min to 34 hr. If they were all equally available, the longer-lived isotopes would obviously be preferred, since the half life is much greater than the time required for most experiments, and since the necessary correction for the decay of the activity becomes small, even negligible. A common empirical rule among radiochemists is that the useful period of tracer activity is four half lives, so that if 10 to 20 min is required for experimental operations, the half life must not be less than 3 to 5 min.

2. The type and intensity of the radiation emitted during decay is of consequence, for the more energetic it is, the more efficient the use of tracer becomes. Isotopes that emit soft beta particles accompanied by no gamma-ray emission are generally unsatisfactory for ready application. Limitations of this sort, however, are not prohibitive, inasmuch as improvements in instrumentation can frequently overcome such difficulties. In general, the best isotope of a given element for tracer purposes is the one that emits energetic gamma radiation.

A second consideration involves the desirability of obtaining high specific activity in the tracers in order that sensitivity in detection and measurement may be realized even with great dilution. In order to meet this demand a large variety of methods for the preparation of "carrier-free" tracers have been investigated. The use of charged wires, ion-exchange adsorption, solvent extraction, coprecipitation methods, Szilard-Chalmers methods, and many other procedures has been described in the literature of the Plutonium Project.²⁰

Two more properties preeminently desirable with tracer preparations for use in analytical research may be mentioned in addition to long half life, energetic radiation, and high specific activity.

First, it is essential that the tracer be obtained in a state of high radiochemical purity. As is the case with the use of fine reagents in exact analysis, so is it important with tracers that a high degree of chemical purity be achieved. Impurities in tracers are usually of a radiochemical nature (i.e., radioactive isotopes of other elements) because of the unavoidable presence of side reactions along with the primary nuclear reaction used to prepare the desired active isotope, or because of inherent limitations in the method of tracer preparation, as, for example, in isolation of tracers from complex fission-product mixtures. Two types of simple tests may be made to establish radiochemical purity: (1) the half life of the tracer may be determined, and impurities of different decay periods may then be easily detected; or (2) aluminum or lead absorption curves may be measured, thus serving to characterize the energies of the beta and gamma radiations that are unique to the tracer isotope. In the case of alpha-emitting radioactive tracers the range of the alpha particles is a very sensitive indication of tracer purity. Beyond doubt the most reliable recourse is a radiochemical analysis of the tracer preparation by means of tested procedures.¹² Chemical purity is of particular importance when radioisotopes are to be used instead of stable isotopes, for then the interference caused by even a trace of impurity is of possible serious consequence.

Second, in the use of tracers of established purity as indicators to reveal the changes occurring in stable isotopes as a result of chemical reactions, etc., it is essential that the chemical "state" of the tracer be the same as that of the carrier. Thus the tracer-preparation method may occasionally result in the presence of the radioelements in oxidation states, hydrolysis states, or in stable complex ions, so that the tracer is chemically different from the added carrier. An example of this effect is to be found in the case of zirconium, in which the tracer is frequently hydrolyzed to a degree quite different from the carrier, and in which "equilibration" is essential and may be achieved by digestion with the carrier in the presence of strong nitric acid.²¹ Iodine tracer and its equilibration with carrier iodine compounds affords another example. Here the equilibration may be carried out by an oxidation-reduction cycle.²² In avoiding difficulties due to a lack of exchange or interchange many different chemical operations may be used, their selection being dependent upon the common sense of the analyst who is aware of such possibilities.

2. ANALYTICAL APPLICATIONS OF RADIOACTIVE ISOTOPES

2.1 Use of Radioactive Indicators in Shortening Analysis Time Required for Complex Samples. In considering the utility of radioactive

indicators in analytical chemistry a number of examples will be cited to illustrate several of the most frequent types of application hitherto performed. One such application is the use of radioisotopes as controls in studies of the efficiency of analytical separations, as in precipitation, electrochemical deposition, solvent extraction, adsorption, and volatility. Occasionally, when the effectiveness of a given separation is thus quantitatively determined, it is possible to carry out appropriate corrections to the assay values, thereby making the use of simplified analytical procedures reliable. In the analysis of complex materials this approach may evidently result in a very great shortening of the time required. The work of von Hevesy and Hobbie²³ on the analysis of lead in rocks from various sources affords an instructive example of the employment of radiometric controls. Their procedure involved the separation of traces of lead from the siliceous mass by the use of hydrofluoric acid, together with the subsequent anodic deposition of PbO_2 , which was determined gravimetrically. They then performed the lead determination colorimetrically. Despite the agreement observed a control on the completeness of recovery was also desired. This control was effected simply by addition of a small quantity of radium D (22-year Pb^{210}) soon after the removal of silica and by the subsequent determination of the radioactivity of the deposited lead. Knowing both the total activity of the radium D added and the activity recovered by electrolysis, they calculated directly the percentage of total lead that succeeded in reaching the anode. Since this percentage corresponds to the fraction of lead actually recovered, the total amount present could easily be determined by correcting for the deficiency in radium D activity. Table 28.1 illustrates the data found and shows the agreement between the various methods of determining lead.

This type of correction procedure may obviously be applied to correct for solubility losses, etc., in many types of analytical determinations.

2.2 Use of Radioactive Indicators in Analytical Separations. Another type of application of tracers is their use in the determination of the completeness of analytical separations, as, for example, in precipitation operations. Thus, in the development of a method for the analysis of rare earths, Myers²⁴ has applied the tracer technique to the determination of the best conditions for the precipitation of rare-earth oxalates. As may be seen from the results given in Table 28.2 below, a more complete precipitation of yttrium oxalate is obtained when operations are conducted at room temperature. Also, slightly more complete precipitation occurs at lower acidity, an observation that is in harmony with the known variation of the solubility of the rare-earth oxalates in mineral acids. Since the precipitate

formed in a hot solution was observed to be coarser and hence more readily centrifuged or filtered, the best procedure, as may be seen from the table, was to cool the mixture and then allow it to digest at room temperature for a short time before further steps were taken.

Table 28.1 — Rock Analyses with Radiometric Control

Type of rock	Weight of sample, g	Pb on anode, g Pb/g rock	Colorimetric determinations, g Pb/g rock	RaD recovered, %	Pb content corrected, g Pb/g rock
Dunite	34.6180	32×10^{-6}	30×10^{-6}	71	42×10^{-6}
Lherzolite	24.6817	15×10^{-6}	13×10^{-6}	69	19×10^{-6}
Granite	48.0611	18×10^{-6}	16×10^{-6}	53	30×10^{-6}
Basalt	28.0984	4×10^{-6}	5×10^{-6}	100	4×10^{-6}
Kimberlite	33.0458	12×10^{-6}	11×10^{-6}	69	16×10^{-6}

Table 28.2 — Tests for Completeness of Precipitation of Yttrium as the Oxalate in Standard Analysis Procedure

Concentration of HCl in solution, normality	Digestion temperature, °C	Digestion time	Y left in solution (57-day Y^{91} tracer), %
0.1	25	20 min	0.5
0.1	25	80 min	0.3
0.1	25	180 min	0.4
0.1	25	26 hr	0.4
0.1	90	20 min	2.2
0.1	90	80 min	1.6
0.1	90	180 min	1.6
0.1	*	26 hr	0.5
0.05	25	20 min	0.5
0.05	25	80 min	0.3
0.05	25	180 min	0.3
0.05	25	26 hr	0.4
0.05	90	20 min	1.2
0.05	90	80 min	1.0
0.05	90	180 min	1.1
0.05	*	26 hr	0.5

*Cooled overnight.

The use of the 6.8-day U^{237} radioisotope may be cited, for it was employed effectively in the study of the recovery of uranium by the precipitation of $(NH_4)_2U_2O_7$ both in the presence and in the absence of oxalate ion.²⁵

One of the most frequently occurring sources of error in gravimetric analysis is caused by the coprecipitation of impurities present in the solution from which the precipitate is formed. Here again radioactive indicators may serve to shorten considerably the time that is needed to determine the magnitude of such effects and to test the efficacy of measures designed to eliminate this interference. In separating cerium from other rare earths, a process in which coprecipitation might be expected to occur readily, Boldridge and Hume²⁶ have made observations on the removal of lanthanum (taken as typical of lanthanum, praseodymium, neodymium, and promethium) from cerium by repeated iodate precipitations of $\text{Ce}(\text{IO}_3)_4$. Lanthanum tracer (40-hr La^{140}) was used, and the activity was first precipitated with 20 mg each of lanthanum and cerium carrier by the addition of hydrofluoric acid. The fluoride precipitates were dissolved in boric and nitric acid, and the cerium oxidation was carried out with 1 g of KBrO_3 and was followed by its precipitation as ceric iodate with iodic acid. The iodate precipitate was dissolved and, either immediately or after reprecipitation, was reduced with peroxide and scavenged with zirconium iodate, as in the standard analysis procedure for radiocerium.²⁷ The cerium was then twice precipitated as hydroxide, converted to oxalate, weighed, and mounted for counting. In short, a complete cerium analysis was performed by varying only the number of ceric iodate precipitations. From the results presented in Table 28.3 it may be concluded that a single ceric iodate precipitation carried 5 to 10 per cent of the lanthanum present. The presence of 20 mg of lanthanum apparently made little difference. Three ceric iodate precipitations are sufficient to reduce the lanthanum contamination to about 0.1 per cent of the original. Interestingly enough, the use of 20 ml of 0.35M iodic acid seems preferable to the use of 2 ml of 3.5M iodic acid.

The removal of yttrium from cerium by repeated precipitations was next determined. Much trouble was encountered from the presence of small amounts of cerium activity in the yttrium tracer (a fact that emphasized the necessity of radiochemical purity in tracer preparations) and cerium salts in the yttrium carrier. After thorough purification of each, an experiment similar to the one described for lanthanum gave the results shown in Table 28.4. The coprecipitation of yttrium was found to be less extensive than the coprecipitation of lanthanum.

The coprecipitation of sexivalent uranium by using a collector precipitate of CaF_2 has been studied by de Haan,²⁸ who used the 6.8-day U^{237} with considerable success. The procedure used in a typical precipitation experiment was as follows: The uranium solution contain-

ing U^{237} tracer was reduced either with ammonium hyposulfite or with zinc amalgam. Calcium was then added, and the solution was heated nearly to boiling, whereupon NH_4F solution was added until it was present in slight excess. The CaF_2 formed was observed to have a tendency to peptize, and it was found that boiling served to coagulate

Table 28.3 — Removal of Lanthanum from Cerium by Repeated Iodate Precipitations

Number of ceric iodate precipitations	La holdback added, mg	HIO_3 added as precipitant	La in the Ce fraction, %	
			Expt. 1	Expt. 2
1	20	20 ml, 0.35M	9.7	10.8
1	20	20 ml, 0.35M	7.1	7.6
2	0	20 ml, 0.35M	0.9	1.0
2	0	2 ml, 3.5M	2.4	3.6
2	20	20 ml, 0.35M	0.8	0.8
3	20	20 ml, 0.35M	0.1	0.1
1*	20	20 ml, 0.35M	4.2	4.4
2*	20	20 ml, 0.35M	0.4	0.8
3*	20	20 ml, 0.35M	0.3	0.2

*The last three sets of samples were run with lanthanum tracer especially purified from cerium.

Table 28.4 — Removal of Yttrium from Cerium by Repeated Iodate Precipitations

Number of iodate precipitations	Y activity in the Ce fraction, %	
	Expt. 1	Expt. 2
1	2.7	2.5
2	0.1	0.1
3	0.02	0.03

it. After centrifuging the precipitate the filtrate was poured off, no attempt being made to wash the precipitate. The beta activity in the resulting filtrate and precipitate was then determined, and the results are shown in Table 28.5.

A few additional experiments were conducted to determine how high the concentration of calcium had to be to ensure more than 90 per cent recovery of the uranium. These experiments were carried out in the same manner as those described above, except that the con-

centration of the collector was varied systematically. As may be seen from Table 28.6, a concentration of calcium of 1 mg per milliliter gave a satisfactory separation.

Radioactive indicators have also found application in analytical separations requiring solvent extraction. In the separation of rhodium from tellurium all the common precipitants for rhodium were

Table 28.5 — Coprecipitation of Uranium(IV) with CaF_2

Weight of uranium, mg	Weight of iron, mg	Weight of calcium, mg	Volume of solution, ml	Uranium coprecipitated, %
40.0	0	50	5	92
0.2	32	10	12	87

Table 28.6 — Dependence of Coprecipitation of Uranium(IV) on Mass of CaF_2 Collector Precipitate *

Weight of calcium, mg	Uranium coprecipitated, %	Remarks
10	71	Partially peptized
50	64	
100	95.5	

*Conditions: 2.2 mg of uranium(IV) contained in 100 ml; zinc amalgam reduction.

found by Ballou²⁷ to carry tellurium. Finally, the extraction of rhodium from alkaline solution by pyridine was found to give the desired separation. When rhodium was extracted from an aqueous solution also containing very small amounts of tellurium as tellurite, the pyridine layer contained 5 per cent of the tellurium. However, a repetition of this experiment with bulk amounts of tellurite present reduced the tellurium contamination in the rhodium pyridine layer a hundredfold.

The electrolytic purification of uranium solutions with a mercury cathode has been studied with the use of uranium tracer produced at the Berkeley cyclotron by Kamen.²⁹ By adding the active isotope to the uranium before the electrolysis it was possible to show that no uranium actually dissolved in the mercury as a consequence of reduction to the metal. A loss of 0.33 ± 0.01 per cent was shown to be caused by entrainment, and it was proved that this amount could be recovered quantitatively by one water wash.

Another of the many potential applications of tracers to analytical technique lies in the ease with which tests for adsorption errors can be made. As has been amply appreciated, such errors are of particular importance in connection with trace analysis. Thus the well-known adsorption of lead or chromium on glassware may be quantitatively estimated, and a suitable correction may be applied if such a procedure is considered desirable.

In this brief survey it has been possible to do little more than mention some of the extremely numerous applications of tracers in

Table 28.7 — Solubility of Lead Sulfate in Sodium Sulfate Solutions

Sodium sulfate concentration, normality $\times 10^4$	Solubility at 23°C	
	Radiometric, normality $\times 10^4$	Analytical, normality $\times 10^4$
0	(2.8)	2.8
5.05	1.27	1.34
7.50	0.99	1.04
10.0	0.81	0.90
25.0	0.56	(0.60)
50.0	0.44	
75.0	0.34	
100.0	0.31	

all varieties of analytical operations. Radioactive indicators have been used repeatedly in the chemical work performed throughout the Plutonium Project for the purpose of making quick, convenient, and effective tests of the efficiency of separation procedures in analytical operations.

2.3 Use of Tracers in Solubility and Kindred Measurements. An important application of radioactive isotopes will undoubtedly take place in solubility measurements. In the determination of the solubility of very slightly soluble substances, tracer methods find wide application. For example, Ferla³⁰ has used radiophosphorus to study the solubility and, hence, the completeness of precipitation of ammonium phosphomolybdate. Rosenblum and Kolthoff³¹ have applied radiolead (10.6-hr thorium B) to the determination of the solubility of lead sulfate in water and in sodium sulfate solutions. A comparison of the results obtained thereby with an established method is shown in Table 28.7.

Although no claims of great accuracy have been made for this method, close approximations to the analytical solubility values were evidently observed. Furthermore, solubility values that are appar-

ently reliable may be determined in regions that are not readily susceptible to customary analytical procedures.

The use of artificially radioactive isotopes in the determination of the nature of analytical precipitates has recently become of increasing importance. The research of Kolthoff and coworkers^{32,33} on the aging of AgCl precipitates may be cited, in which the 37-min Cl³⁸ was used, and on the aging of AgBr, in which the 4.4-hr Br⁸⁰ was used. Langer³⁴ has found the 45-day Ag¹⁰⁵ of use in studies of the thermal aging of both the above-mentioned silver halides.

3. ACTIVATION METHODS FOR ANALYSIS OF TRACE IMPURITIES*

The presence of certain elements in a sample that is to be analyzed can often be established, with or without the aid of a chemical separation, by means of their characteristic half lives after the substance has been activated in some manner, as, for example, with neutrons, deuterons, protons, or alpha particles. In rare instances, moreover, the analysis can be made without destroying or even changing the form of the sample. Von Hevesy and Levi³⁵ have applied this method of analysis to the rare-earth elements, where it is especially useful because of the extreme difficulty in applying ordinary analytical procedures. In one experiment they found the 2.5-hr dysprosium period in a sample of yttrium after activation with neutrons, a fact that showed the presence of dysprosium impurity to the extent of 1 per cent. Neutron activations of gadolinium samples were also used as tests for small amounts of europium impurities by means of the 9.2-hr europium period. In connection with fission-product researches Marinsky³⁶ was able to demonstrate the existence of impurities in a sample of praseodymium by the appearance of a decay period of more than 19.3-hr half life after neutron bombardment. In addition, samples of samarium, neodymium, and europium have been shown to be more than 99 per cent pure by means of (n, γ) reactions. Semiquantitative analyses by means of this technique have been conducted by King and Henderson,³⁷ who were able to detect less than 1 part in 10,000 of copper in silver by bombarding the silver sample with alpha particles.

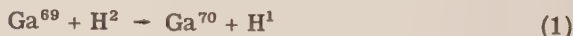
It must be pointed out, however, that extreme care must be exercised in the application of these sensitive methods to analysis. As Seaborg³⁸ has indicated, this is especially true when a sample is bombarded with deuterons, protons, or alpha particles because of the danger that small amounts of impurities may be introduced from re-

*See paper by G. E. Boyd.⁴⁵

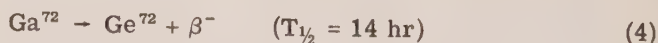
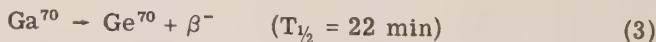
coil atoms and volatilization in the target chamber. Even when samples are bombarded through a window with the target outside the acceleration apparatus, care must be taken to prevent the introduction of extremely small amounts of impurities during the preparation of the target. Although many of these complications are absent when neutron activation through radiative capture is employed, the possibility of the occurrence of competitive reactions such as $(n,2n)$, (n,p) , and (n,α) must be borne in mind. Furthermore, interferences caused by the occurrence of daughter growth from the decay of reaction products must be eliminated.

A quantitative estimate of the amount of the element impurity can be made in those instances in which the yield of the reaction involving the formation of the radioactivity has previously been determined. An excellent example of the effectiveness of this method has been afforded by the work of Seaborg and Livingood,³⁹ who were the first to suggest this new, sensitive method of analysis. A description of one of their experiments merits presentation in some detail.

When a sample of iron was bombarded with deuterons, it was found that two of the radioactivities produced could be attributed to an extremely small amount of gallium impurity in the iron. This was established by the fact that the half lives of the two beta-emitting activities, 22 min and 14 hr, were identical with the known half lives of Ga^{70} and Ga^{72} , respectively. A chemical separation according to the methods of Noyes and Bray⁴⁰ was performed upon a sample of bombarded iron, to which a small amount of inactive gallium (i.e., "carrier") had been added after the bombardment. The 22-min and 14-hr periods appeared only in the gallium fraction. The radioactive isotopes were formed according to the reactions

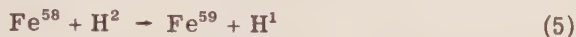


and decayed as follows:

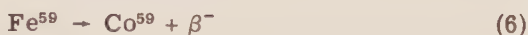


It would be possible to make an accurate estimate of the amount of gallium impurity in the iron if the cross section of reaction 1 or 2 were known, but the yield of these reactions has not been determined. However, an approximate estimate of the amount can be made by comparing the initial intensity of Ga^{70} or Ga^{72} with the initial intensity

of another radioactive isotope formed by the same type of reaction and under the same conditions from an isotope of known concentration. It has been established by chemical separations that one radioiron isotope (in addition to several radiocobalt and radiomanganese isotopes) is produced when iron is bombarded with deuterons, and that this radioiron activity is due to Fe^{59} produced according to the reaction



The Fe^{59} emits beta particles and decays with a half life of 43 days, as follows:



Iron and gallium were separated together by an ether extraction from a sample of iron that had been bombarded in the cyclotron for 45 min with $50 \mu\text{a}$ of deuterons with 6.4 mev of energy. The initial measured activities of the 22-min Ga^{70} , 14-hr Ga^{72} and 43-day Fe^{59} , as measured with a Lauritsen-type quartz-fiber electroscope, were 0.12, 0.0033, and 0.10 divisions per second, respectively. After correction to infinite bombardment time, which may be done through the relation

$$N_0 = N_\infty (1 - e^{-0.693t/T_{1/2}}) \quad (7)$$

these initial activities become 0.16, 0.091, and 217 divisions per second. These corrected initial activities should be proportional to the concentrations of Ga^{69} , Ga^{71} , and Fe^{58} in the bombarded iron.* It is known that the concentration of Fe^{58} in iron is 0.5 per cent and that gallium is composed of 61.2 per cent Ga^{69} and 38.8 per cent Ga^{71} . Therefore the corrected initial intensities of Fe^{59} and of either Ga^{70} or Ga^{72} , together with these abundance ratios, lead to a concentration of 6 ppm of gallium in the bombarded iron. One-tenth as much could readily have been detected.

As to neutron reaction procedures, the high fluxes now available make this method of analysis quite feasible in certain circumstances, particularly when the cross section is large. At present, however, a considerable amount of work remains in order to establish the reliability of this method of analysis.

*This assumes that the cross sections of reactions 1, 2, and 5 are equal. They should be almost equal for elements of nearly the same atomic weight.

An instructive example of the use of the activation method when neutrons were employed has been afforded by the experiments of Swartout,⁴¹ in which the isotopic composition of a sample of copper from the calutron was determined. Mass-spectrographic analyses had indicated 97 ± 1 per cent Cu^{63} and 3 ± 1 per cent Cu^{65} in a sample received. A quantity of this preparation weighing 0.026 mg was irradiated in the pile to form both the 12.8-hr Cu^{64} and the 5-min Cu^{66} . By following the radioactive decay of this sample, together with the flux of neutrons and the isotopic cross section for Cu^{65} , a calculated value of 9.3×10^{-7} g of this mass was initially contained in the sample. Thus a figure of 3.5 per cent Cu^{65} was deduced, which is in better agreement with the spectrographic value than would be expected owing to the approximate nature of the flux and cross-section values employed.

4. RADIOMETRIC METHODS OF ANALYSIS

As was mentioned at the beginning of this chapter, two basically different types of radiochemical analysis are known. The first type, radiometric analysis, involves the determination of the weight of an element by measuring its radioactivity, with previous knowledge of its specific activity. In this manner the weight of natural uranium present in a mixture can be determined by isolating the uranium free from other radioactive elements and counting the alpha activity. This method is closely analogous to colorimetric and volumetric determinations. The second type of radiochemical analysis, activity analysis, involves the determination of the radioactivity due to a given element in a mixture of radioactive elements. The results may be expressed as absolute activity or in terms of percentage of the total mixed activities due to the element in question. In this section only the former type of analysis will be considered. For a full discussion of the technique of activity analyses, the reader is referred to various volumes in Division IV of the National Nuclear Energy Series.

4.1 Analysis for Uranium. (a) Determination of Uranium in Ores and Ore-refinery Intermediates. (1) Gamma-count Method. A rapid, accurate method⁴² for the determination of uranium when present in ores has been devised on the basis of a measurement of the gamma activity exhibited by such samples. No chemical separations whatever are required here, and the experimental arrangement for the activity assay can be made extremely simple. However, the method is not in itself absolute, since the prior measurement of samples of known U_3O_8 content must be carried out and a calibration curve must be obtained. Preliminary studies have demonstrated the procedure to be applicable with ores containing 0.1 to 60 per cent U_3O_8 .

Although the results thus far have been obtained by means of a Geiger-Mueller counter with its auxiliary a-c circuits, it is by no means necessary that such equipment be employed. Sensitive electroscopes or other integration measuring instruments, such as ionization chambers, may be used equally well.

Several requirements are imposed upon this method of analysis. In the first place, an examination of the U^{238} decay series shows that any determination of uranium based on gamma activity is actually made on the radiation emitted by RaB and RaC, which are in radioactive equilibrium with their radium progenitor. From these considerations it follows that the uranium/radium ratio in a given ore must be accurately known. Experiments with ores of the same type, such as were employed in the development of this gamma-count method, seemed to indicate that a normal secular equilibrium existed, so that a value of 3.4×10^6 for the uranium/radium ratio was assumed. An accurate determination of the radium content may be made by using the procedure of Curtiss and Davis,⁴³ which was devised and is in routine use at the National Bureau of Standards. A second limitation arises because of interference. Since the thorium family also includes elements that emit hard and intense gamma radiations, the amount of thorium in the ores must be known. In many instances the amount present is so small that its effect may be safely neglected. If such is not the case, then the uranium determination will require a special calibration. Finally, in the method as it now exists a considerable effect is caused by the scattering of the quantum radiations. In the future design of gamma-ray assay equipment some attention should be directed to reducing this factor to a minimum.

Although reference to the original publication is recommended for potential users of this method, it is possible to present an abbreviated procedure at this point. The powdered sample of ore, which has been dried at 105°C , is first spread on glazed paper and thoroughly mixed. A suitable container is then filled with 50 to 100 g, and the sample is weighed to the nearest centigram. Gamma-count readings are taken at 10-min intervals and are so repeated as to ensure a statistical accuracy of 0.3 per cent or better (the statistical accuracy is computed according to the usual formula). These gamma-activity readings are corrected for chance coincidences, background, and any variation in counting sensitivity and are then expressed in counts per second per gram of ore. The important self-absorption correction must next be made either by direct measurement or by a procedure known as the "mass-absorption method," which, in the interests of brevity, will not be described here. Finally, the percentage of U_3O_8 contained in the sample may be read from a calibration curve in which the corrected gamma counts per second per gram are plotted against the

percentage of U_3O_8 , or the corrected observed activity may be multiplied by a previously determined specific activity factor that has been expressed in gamma counts per second per gram of U_3O_8 .

A comparison of results from the gamma-count procedure with chemical analyses is afforded by Table 28.8.

Table 28.8 — Uranium Determination on Standard Series

Sample No.	U_3O_8 content, %		
	Chemical analysis*		Gamma-ray method†
	Lab. A	Lab. B	
1	18.69	18.70	18.61
2	13.90	13.91	13.76
3	26.82	26.81	26.80
4	35.48	35.55	35.75
5	29.76	29.78	29.57
6	27.69	27.74	27.84
7	1.34	1.35 - 1.36	1.36 ₆

*National Bureau of Standards method.

†Gamma activity counted through 6.5-mm lead absorber.

These results show good agreement between the physical and chemical measurements. Moreover, since the materials studied varied widely in their specific gravities (i.e., different mean atomic numbers), it may be assumed that the method of correction for self-absorption was valid.

(2) Alpha-count Method. An alpha-count method analogous in many ways to the gamma-count procedure just described has been employed for the estimation of uranium. However, owing to the nature of the samples to be analyzed some chemical operation is required which will both separate and concentrate the uranium. In the present procedure use is made of a "collector technique," wherein a fixed amount of collector precipitate (hydrous ferric oxide) is formed which carries down the uranium as $(NH_4)_2U_2O_7$. This operation is followed by centrifugation, evaporation, ignition, and alpha-count determination using an air-filled ionization chamber. The procedure in its entirety affords one of the quickest methods for determining the amount of uranium in samples that it would be tedious to analyze by other methods. The weight percentage of uranium is obtained from alpha-assay and weight data by means of a calibration curve. In general, however, the method is applicable only when the requirements for accuracy are not too high. Thus, a comparison of the values obtained in the extremely

rapid method for the analysis of uranium by the alpha-count method with results obtained by more accurate methods indicated that a value less than one-half or more than twice the correct value was hardly ever observed by the former method, provided that the isotopic assay and the nonvolatile content of the samples varied by no more than ± 15 per cent and the counting error was no larger than ± 15 per cent. The precision on duplicate samples was found to lie between ± 5 and ± 10 per cent.

Since 1 g of natural (i.e., unchanged) uranium emits 25,000 alpha particles per second, one-half of which may be counted, 6.7γ will give 5 counts per minute, which is far enough above the usual background of 1 to 2 counts per minute to be decisive. However, owing to sample self-absorption effects on the part of the carrier and to other factors the practical lower limit has appeared to be about 25 ppm of uranium. The alpha-count method is evidently usable for the analysis of samples containing up to 1 per cent uranium, although its most frequent use has probably been with solutions containing 0.01 to 0.05 per cent of this constituent.

It is obvious that the success of the procedure will depend upon the absence of all alpha emitters other than the uranium isotopes. Due caution should be exercised to avoid chance contamination of the samples.

To assay the amounts of alpha activity, a high-voltage air chamber with parallel-plate electrodes at a distance of 1 cm can be used. As was pointed out in an earlier section, a counting geometry of about 50 per cent may be realized with such a chamber when an operating voltage of 1,200 to 1,500 volts is maintained between the plates. In addition to the high-voltage supply the auxiliary equipment should include a scaling circuit, recorder, and timer capable of recording 20 to 5,000 counts per minute. The entire assembly must have a background of less than three pulses per minute. Great care must be taken to prevent the contamination of the counting chamber.

Before describing the procedure, brief mention of the preliminary studies that served to establish the method is worth while. Thus, in order to be able to count the alpha activity in a reproducible medium, it was thought advisable to bring the uranium(VI) down on the same solid matrix from each sample so that the effect of self-absorption of the alpha particles would be nearly the same from determination to determination and could be effectively eliminated by a calibration of the method. For this reason it was decided to add an amount of iron(III) as collector that would be large in comparison with the quantity of iron already present in the sample taken and then to coprecipitate the uranium with hydrous ferric oxide by the use of NH_4OH .

Iron was picked as the carrier inasmuch as earlier work had demonstrated that the carrying of minute amounts of uranium by " $\text{Fe}(\text{OH})_3$ " was quantitative.

The following procedure for the analysis of centrifuge effluent concentrates (C.E.C.) is typical of the alpha-count uranium-assay method:³³ Into each of two 3-ml centrifuge tubes are pipetted 1.00-ml samples of the C.E.C. selected, followed by the delivery of a third volumetric sample into a previously tared weighing bottle and its subsequent weighing. To each centrifuge tube is now added 25 mg of

Table 28.9 — Comparative Accuracy of Alpha-count Method for Determination of Uranium

C.E.C. sample	Alpha-count method, %	Peroxide colorimetric method, %	Pentaether method, %
1	0.032	0.037	
2	0.024	0.030	
3	{ 0.015 } { 0.016 }	0.022	{ 0.016 } { 0.017 }

iron(III) as ferric chloride in a solution containing 50 mg per milliliter. The tubes and contents are heated nearly to boiling on a water bath and are then cooled rapidly under running water. Precipitation of the iron is carried out by the addition of concentrated NH_4OH from a dropper, accompanied by vigorous stirring with a 25-gauge platinum wire of suitable length. The tubes are then centrifuged, and the supernatant liquid is withdrawn by means of a capillary-tipped transfer pipet with a syringe control. The precipitate in each tube is then washed twice with dilute NH_4OH , each wash being followed by centrifugation. Next the resultant solids are slurried into a 25-ml platinum-crucible lid, evaporated to dryness under an infraradiator, ignited in a muffle furnace for 15 min at 850°C , cooled, and then counted. The counting interval selected was 4 min, and activity determinations were performed and checked for each sample. After correction for coincidences, background, and any variation in counter sensitivity, the counts-per-minute data are divided by the weight of sample taken, which is normally 1.2 to 1.4 g, and the resulting figure for counts per minute per gram of C.E.C. is used to compute the weight percentage of uranium in the initial C.E.C. sample. The specific activity from the calibration curve was 6,847 counts per minute per gram of C.E.C. per % of uranium.

A comparison of this radiometric procedure with various chemical methods for uranium analysis is given in Table 28.9.

One point worth noting in Table 28.9 is the fairly constant difference of 0.006 per cent between the count and peroxide colorimetric analyses. A further observation shows that the alpha-count method is singularly free of the difficulties introduced to the normal chemical analysis of a C.E.C. sample by the presence of small amounts of impurities such as molybdenum.

As a final check on the quantitative carrying of sexivalent uranium by the gelatinous hydrous ferric oxide, two of the ammonia effluents from a typical C.E.C. determination were evaporated onto platinum-crucible lids, ignited, and counted. A negligible count was obtained in each case.

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Chapter 29

OTHER METHODS

Part A

CHROMATOGRAPHIC ADSORPTION METHODS OF QUANTITATIVE SEPARATION

By J. Schubert

Numerous applications of various chromatographic techniques to inorganic analytical chemistry have appeared in the literature. Unfortunately, the actual reductions to practice have been limited in scope and have often suffered from many disadvantages, such as the necessity for extensive treatment of solutions before passage through the column and the need for long operation times as well as extreme care in the preparation of the adsorbent-packed column.

The comparatively recent introduction of ion-exchange resins¹ has resulted in efficient, simple, and rapid chromatographic methods. A considerable amount of development work has been done on the Project in connection with the recovery of radioactive elements and in analytical separations. These separation methods have been particularly successful with radiochemical concentrations of cations on the order of 10^{-10} M. The genesis of much of this development was the pioneer adsorption work of G. E. Boyd and his associates (see various volumes in Division IV of the National Nuclear Energy Series).

The principal service of column adsorption methods to analytical chemistry is that of providing a relatively simple means of separating an element in a sufficiently pure state in order that, for example, a direct precipitation, ignition, and weighing will suffice to complete the quantitative analysis. No organized evaluation and synthesis of the data have been made for the purposes of applying the findings as a technique in analytical chemistry. Although a large amount of information concerning adsorption methods for the separation and concen-

tration of cations exists, exact procedures have not been developed for a large variety of separations. Accordingly, an attempt will be made to include general information of such a nature that it can serve as a guide to the experimenter in this relatively undeveloped field. The material to be presented will include (1) general principles, (2) nature of the adsorbents, (3) experimental techniques, and (4) examples of the separation and concentration of different cations. The separation of the individual members of a series from one another, such as in the alkaline earths and the rare earths, will also be treated.

Some terminology used in column work is as follows:

1. Elute: to wash out
2. Elution: the separation of material by washing
3. Eluate or eluant: collectively, the washings obtained by elution
4. Adsorption: a term employed to describe the retention or extraction of cations by the ion exchanger even though it is understood that base exchange is not a purely surface phenomenon
5. Desorb: a synonym sometimes used interchangeably for elute
6. Effluent: that which flows out
7. Influent: that which flows in
8. Breakthrough: the point at which the capacity of the bed for any single cation is reached

1. PRINCIPLES GOVERNING ADSORPTION

1.1 Mechanism of Ion-exchange Adsorption. The nature of the adsorption on cation-exchange resins is similar to the action in other substances which possess cation-exchange properties, such as the inorganic zeolites. Synthetic cation exchangers with which the most successful separations have been accomplished will be used to illustrate the principles of ion exchange. A cation exchanger may be considered to behave as a porous salt containing an insoluble anion and exchangeable cations. When the exchanger is immersed in a solution of cations, a competition for the available positions in the solid takes place between the replaceable cations present in the exchanger and those in the surrounding solution.

The synthetic-resin cation exchangers are condensation products of the polyhydric phenols and formaldehyde with either nuclear or methylene sulfonic acid groups incorporated to increase the adsorption capacity in the low pH regions. A possible type of polymer is shown in Fig. 29.1 to indicate the general nature of these exchangers.

1.2 Equilibrium Adsorption Principles. It has been shown² that the exchange adsorption of monovalent cations by a synthetic resin obeys the law of mass action when (1) the activities of the solid-phase components are expressed in terms of their mole fractions, (2) when

the thermodynamic activities of the ions in the solution are employed, and (3) when the anionic part of the adsorbent is assumed to behave as if it were monovalent.

In general, the more highly charged cations are more strongly adsorbed. For example, the order of adsorption at a constant pH is $\text{La}^{+3} > \text{Ba}^{+2} > \text{Na}^{+}$. Additionally, for any given series of cations of

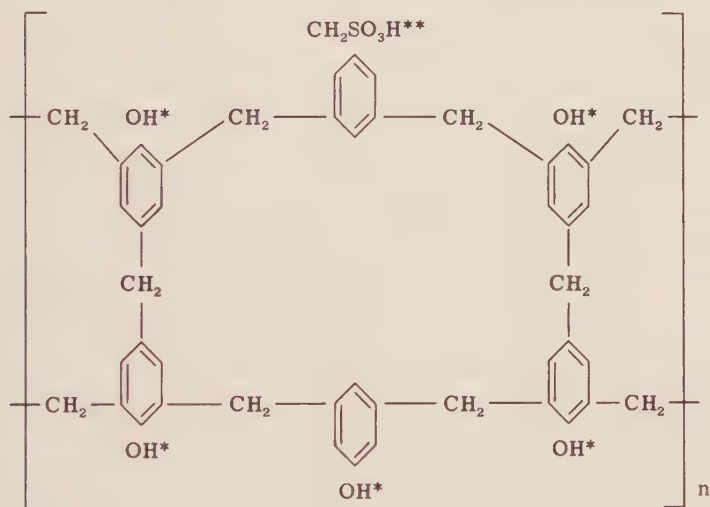


Fig. 29.1—Structural formula for a polymer of a synthetic-resin cation exchanger. Available positions for cations are indicated by asterisks.

the same charge, the adsorption affinities increase as the hydrated ionic radii decrease.³ Hence the adsorption affinities of the bivalent cations, for example, are as follows: $\text{Ba}^{++} > \text{Sr}^{++} > \text{Ca}^{++}$.

The relation between K_a , the thermodynamic equilibrium constant, and the adsorption affinity of the participating cations is evident. Relative adsorption affinities of ions can be determined by equilibrium experiments.

1.3 Adsorption under Nonequilibrium Conditions. When a solution containing polyvalent cations is passed through a column packed with a synthetic cation-exchange resin, differing amounts of the cations are removed depending upon the pH, complexing agent, rate of flow, and such factors. The breakthrough of any ion will depend upon its affinity for the resin. Schematically, the breakthrough of the cations Ba^{++} , Sr^{++} , and rare earths is shown in Fig. 29.2. The shape of the breakthrough curve and the observable point at which it occurs may

be expressed according to the mass-transfer theory^{4,5} as a function of two variables, which depend on chemical as well as physical factors.

An increase in the magnitude of any of the following results in a decrease in the adsorptive capacity of the resin bed and consequently

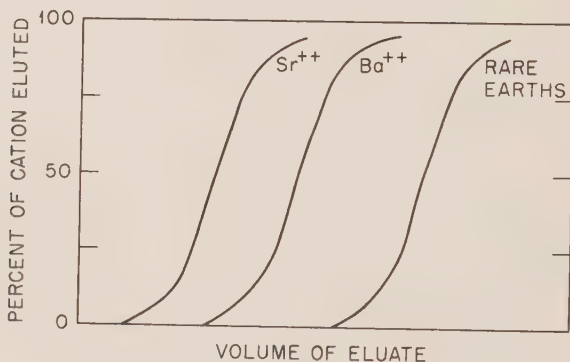


Fig. 29.2—Order of elution. The bed is of Amberlite IR-1.

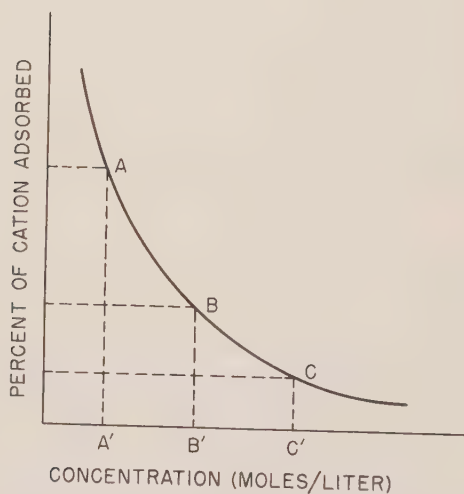


Fig. 29.3—Effect of concentration on fraction of cation adsorbed by cation exchanger.

in an earlier breakthrough: (1) particle size of adsorbent, (2) ionic strength, and (3) temperature. The decrease in capacity associated with temperature is usually of the order of 1 to 2 per cent for each degree of rise above room temperature.

Ordinarily, changes in bed height and column diameter do not affect the performance of the column. The presence of large amounts of undissociated reagents in a solution has no appreciable effect unless it complexes the solution cations.⁶

One method of greatly increasing the capacity of a column for a trace substance in the presence of bulk electrolyte is by diluting the influent. The experimentally observed relation between concentration of a cation and its percentage adsorption is shown in Fig. 29.3.

2. EXPERIMENTAL PROCEDURES AND TECHNIQUES

2.1 Adsorbents. The types of adsorbing materials that may be employed are best classified in a general manner according to the nature of the adsorption.

(a) Cation-exchange Adsorbents. In this group are the inorganic zeolites, such as the sodium-alumina silicates, the newer organic exchangers, which include the sulfonated coals, and the synthetic phenol-formaldehyde resinous adsorbents.

Three widely used products in the latter class are known by the trade names "IR-1," "IR-100," and "IR-100H." Although the principles governing their operation are similar, they differ in two main respects, namely, storage capacity and color throwing.* The capacity and color-throwing properties are in the order IR-1 > IR-100 > IR-100H. For general use IR-100 is quite satisfactory.

The advantages possessed by the synthetic-resin exchangers are as follows: (1) fairly well-defined chemical structure, (2) slight mechanical attrition, (3) large adsorptive capacity, (4) equilibrium adsorption independent of mesh size, and (5) operability with low pH solutions.

The Amberlite exchangers show a nearly linear increase in adsorptive capacity with increase in pH, apparently because more groups are rendered capable of undergoing exchange.⁷

Information concerning the physical properties of the resinous ion exchangers has been given by Myers⁸ in a survey dealing with the properties of synthetic organic exchangers in general. An excellent article on inorganic exchangers has been provided by Walton.⁹ A comprehensive general discussion of types of adsorbents has been prepared by Russell.¹⁰ Sussman and Mindler¹¹ have provided an extensive summary of the literature with 69 references on the various applications of ion exchange.

(b) Anion-exchange Adsorbents. Synthetic resins with anion-exchange properties can be made by condensing aromatic amines with

*Color throwing refers to the color developed as a result of dissolution of a trace of resin that has no effect on the performance.

formaldehyde.⁸ The anion exchange and regeneration of anion exchangers¹² are illustrated by the following equations:



where R represents one or more alkyl or aryl groups or hydrogen. In addition to their use for separating simple anions, anion-exchange adsorbents may be used for the recovery of metals such as chromium, gold, iron, molybdenum, palladium, platinum, and vanadium, which can be converted to soluble anion complexes.¹³ Concentration gains of more than 20 times have been attained. Recovery of such adsorbed anions by elution with alkaline solutions or direct ashing of the resin has been found effective.¹²

(c) Miscellaneous Adsorbents. In addition, a large variety of materials that have been used in the past may prove useful on special occasion. The most important of these are the activated aluminas, which presumably are capable of exhibiting exchange adsorption by virtue of the presence of small amounts¹⁴ of $NaAlO_2$. Chromatographic adsorption columns employing this material have been tested in connection with the problem of the detection of small amounts of uranium, and a minimum amount of about 20 γ was required.¹⁵ Therefore there was no advantage in this method over existing microchemical procedures for the estimation of uranium. Neither do these solids appear to be of value in separating inorganic cations. Jacobs and Tompkins¹⁶ in recent comprehensive adsorption studies with alumina state: "... It is clear that alumina is unsuitable as an adsorbent for inorganic chromatography, particularly for semiquantitative work, since the irreversibility of adsorption and other factors emphasizes the loss of sharpness at both edges during development and renders measurement of widths of bands of no great value. Similarly, the separability of cations becomes more difficult if not impossible"

Silica gel has been used to some extent in inorganic chromatographic analysis also, and possibly its adsorptive capacity is due to the formation of metallic silicates. Other substances such as Fuller's earth, bentonite, and charcoal are known to show base-exchange adsorption of a limited sort which may be attributed to the presence of specific groups or to structurally incorporated impurities.

The organic reagent 8-hydroxyquinoline, known to form highly stable inner complexes with many cations, may be used as an adsorbent in a column procedure¹⁷ by mixing the finely powdered chemical with a nonadsorptive, siliceous filter aid. The order of cation

adsorption parallels the solubilities of the cation quinolates, and very sharp separations have been observed.

2.2 Apparatus and Preparation of Column. For most purposes pyrex-glass tubing is a satisfactory structural material. An excellent

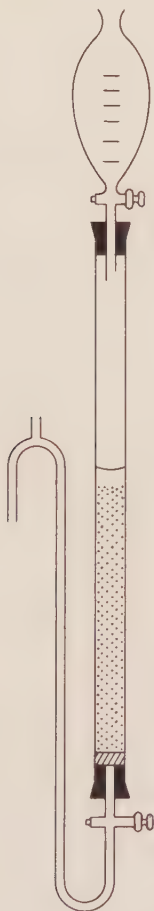


Fig. 29.4—Adsorption column.

support for the adsorbent bed is provided by glass cloth of $\frac{1}{32}$ in. thickness or less. A circular piece of the glass cloth is placed over a one-hole rubber stopper fitted with a glass stopcock. The end that contains the glass cloth is inserted in the column in such a manner that part of the overlapping glass cloth is fastened between the glass

walls of the column and the inserted rubber stopper. One type of column setup is shown in Fig. 29.4.

Depending on a given set of conditions, many variations in column design are possible. Burets of 25 or 50 ml volume containing 3- to 6-in. adsorbent beds can often be used. A description of the various types has been given in a book on chromatography by Strain.¹⁸ A reflux type of column which involves the reuse of an acid eluant is described by Frizzell.¹⁹ Frequently a separatory funnel inserted directly at the top of the column serves as a storage tank instead of more elaborate equipment. Introducing a flowmeter at the outlet is convenient whenever accurate control of the flow rate is desired.

The resinous adsorbent, before use, is air-dried (never oven-dried),² ground in a ball mill, and classified by sieving to the desired mesh size. Generally, the smaller the adsorbent-particle size the better, although 60 to 80 mesh is a good operating range. A slurry of the resin is poured into the column, which is partly filled with water. The "fines" are washed out completely by backwashing the resin bed. This is done by forcing water through the bottom of the column, hence raising the bed. Upon settling, the fines that remain at the top are washed out by raising the bed sufficiently so as to float them out. When the fines are completely removed, the bed is allowed to settle and is then ready for conditioning. The resin bed is freed from traces of cations by passing strong HCl (about 1 to 1) through the bed.

Before use, it is desirable to "condition" the resin bed by running one or more regenerative cycles, i.e., alternative HCl-NaCl-HCl cycles. Naturally, the cation form in which the resin is left is optional.

2.3 Analytical Separations. (a) Cationic Displacement. By utilizing differences in adsorption affinities, it is possible to use a second cation to elute an adsorbed cation or group of cations, the second cation remaining on the column. Upon increasing the concentration of the eluting cation, further removal of adsorbed ions may be effected. The optimum concentration of the eluting cation depends to a large extent upon the magnitude of the equilibrium constants involved. Myers⁵ has proposed that displacement reactions be used in order to shorten analytical procedures by reducing them to simple acidimetric titrations. Thus, with aqueous solutions of bivalent copper which contain only very small amounts of other cations, an adsorption column in which the reaction



occurs may be employed in the determination of this metal by titrating the displaced acid in the effluent from the column. Unfortunately,

there are no quantitative data available by which the feasibility of this idea may be judged.

(b) Complex-ion Formation. Reagents that form slightly dissociated soluble complex ions with cations have been used to improve adsorption separations greatly. The separations are based on differences in the stability of the complex ions formed and on the fractionating action afforded by an adsorbent when employed in a column arrangement. Thus, for example, a nearly complete separation of trace amounts of barium and strontium from each other has been realized by first adsorbing their cations at the top of a deep bed of ion-exchange adsorbent followed by washing with an aqueous 5 per cent ammonium citrate solution adjusted with ammonia²⁰ to a pH of 5.0.

Since many complexing agents are weak organic acids, it is possible to effect highly selective desorptions by appropriate pH control. However, the added eluting properties furnished by the cation component of the complexing agent must not be forgotten. The importance of adjusting the pH of solutions containing complex ions such as citrate so as to obtain efficient removal of adsorbed cations has been exemplified in a striking fashion by the separations of the rare earths in adsorption columns. In the separation of radioyttrium and radio-cerium²⁰ an excellent fractionation was found if the 5 per cent ammonium citrate eluant was carefully maintained in the pH range 2.75 to 2.85; otherwise a much lower radiochemical purity of the fraction was obtained. The recent advances²¹ in the production of gram quantities of extremely pure neodymium using adsorption techniques illustrate the analytical nature of the separations that may be achieved when optimum conditions are found.

The formation of complex metallic oxalato ions has been used in the separation of radiozirconium and radiocolumbium in adsorption columns.²⁰ Recently²² the successful fractionation of protoactinium from macro amounts of zirconium, titanium, and iron has been effected through the use of oxalic acid solutions at various concentrations and pH values.

On the other hand, Kozak and Walton²³ have reported that the binary mixtures Cu + Ni, Cd + Zn, and Ag + Cu were not separated when solutions containing their stable amino-complex ions were passed through deep beds of an organic base exchanger.

2.4 Investigating Possible Chromatographic Procedures. An example may serve to illustrate a method of systematically exploring a possible process utilizing cation exchange. It may be assumed that the problem consists in the separation of the cations yttrium and cerium in an acidic solution containing these cations in trace amounts. One procedure consists in the complete adsorption of both elements

followed by successive selective elution of each. Dilute ammonium citrate will elute yttrium and cerium but at different rates, depending on the pH. In order to determine the optimum conditions, the following procedure may be used.

Several, perhaps five, small columns having a capacity of about 10 or 20 ml and having a length of about tentimes that of the width should be prepared. The capacity or breakthrough point of yttrium and cerium can be determined by passing a volume of solution through and collecting aliquot portions. From the breakthrough point the volume necessary to effect complete adsorption at the particular concentration used can be determined. For the best results it is preferable to have most of the cations adsorbed in the top section of the column.

To determine the optimum pH of the eluting citrate solution, identical volumes containing yttrium and cerium are first passed through each of the five columns, conditions such as flow rate being kept constant. Then ammonium citrate solutions of various pH's are passed through the columns to elute the yttrium and cerium. Aliquot portions are collected and analyzed. Since the ammonium citrate influents differ only in the pH, an appropriate plotting of the results usually reveals a pH region in which most of one ion, yttrium in this case, can be removed while the second ion remains on the column. By increasing the pH the bulk of the second ion, cerium in this case, can be removed.

The preparation of pure radioyttrium and radiocerium has been put on a routine basis by Cohn and coworkers,²⁰ who have described their work in detail. On the basis of this work, Spedding et al.²¹ have evolved methods for separating macro amounts of yttrium from cerium. Their experimental procedure, described in considerable detail, furnishes an excellent illustration of the general experimental approach described above. The nature of some of the alkaline-earth citrate complexes has been described by the author.

In studying variables it is expedient to employ a number of identical columns. A series of experiments can then be simultaneously performed to study one variable while others are held constant. Once optimum chemical conditions are established, the effect of mechanical factors such as flow rate and bed height can be studied and correlated. The application of the mass-transfer theory enables the column performance to be extrapolated over a wider range of conditions than a purely empirical approach allows.

2.5 Separation-Concentration Schemes for Cations. (a) Metathesis Procedures. A frequent problem in analytical chemistry is the separation of cations from anions before the final determination. Although metathesis reactions are common to most analytical separa-

tions on adsorption columns, two particularly efficient ones will be described.

Frizzell¹⁹ has accomplished excellent separations of anions and cations using the adsorber Zeo-Karb, a sulfonated coal product. In the case of copper sulfate the equation for quantitatively separating the copper from the sulfate ion is



where R is 1 equivalent of adsorber. The adsorber was washed with water, and the sulfate was determined in a solution containing only one cation, namely, hydrogen ion. The copper was eluted from the adsorber with hydrochloric acid and determined in the resulting solution. Separations of the cations and anions in solutions of ferric chloride, sodium oxalate, ammonium dihydrogen phosphate, and calcium borate were obtained which were quantitative within the accuracy of the methods used to determine the various ions. It was found that successful separations were obtained when the total ion concentrations were small and the pH was between 2 and 4.

(b) Concentration of Metal Traces. The use of zeolites in the concentration of metal traces offers promise, although little work has been done in this direction. Abrahamczik²⁴ has shown that by permutit exchange minute amounts of iron can be isolated and determined. Ten liters of distilled water containing 0.0025 ppm of ferrous iron was run through a 50- by 450-mm column of "neopermutite" (about 400 g). One hundred milliliters of warm saturated sodium chloride solution was then passed slowly through the column in the reverse direction, followed by 150 ml of wash water. Iron was determined colorimetrically in an aliquot of the combined solutions, and 90 per cent of that added was found.

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Part B

GAS ANALYSIS

By F. E. McKenna

Gas mixtures are usually analyzed by successive absorptions of the various constituents, or in some cases nonabsorbable gases are burned to form gases that can be absorbed. When a large number of analyses must be made on a routine basis, an Orsat or related absorption apparatus is not very satisfactory because of the time required. In the case of binary gas mixtures rapid and accurate results can be obtained by measuring the thermal conductivity of the mixture. Such a method becomes particularly useful when neither component is absorbable. Typical binary mixtures that have been analyzed conductimetrically are helium-carbon dioxide, oxygen-nitrogen, and nitrogen-helium. Multiple-component gas mixtures may be separated by fractional condensation at temperatures at which the vapor pressures of certain components are less than 0.1 mm Hg. Some gases, such as water vapor, have been analyzed by specific methods.

3. ORSAT APPARATUS

In using the conventional Orsat apparatus, the gas buret is a satisfactory sample device for large numbers of routine analyses that do not require an extremely high degree of accuracy. A saturated aque-

ous solution of sodium chloride colored with methyl orange is a more satisfactory confining liquid than mercury because of greater ease of manipulation.^{1,2}

The conventional types of Orsat apparatus were used without modification. Some observations were made, however, which are usually not emphasized in discussions of Orsat procedure.

The solubility of carbon dioxide in a saturated sodium chloride solution is sufficiently small to be negligible for most of the samples and for contact times not exceeding 2 or 3 min. There have been indications of a solubility of the gases, notably carbon dioxide, in the surface film of the confining liquid. If, after the volume of the gas in the buret is apparently constant, the attached leveling bulb is agitated, a decrease in volume may be immediately observed. This effect is sufficiently large to cause a 2 per cent decrease in volume over a period of 40 min.

It was found experimentally that, by allowing 3.00 ± 0.25 min before reading the gas volume, the drainage and solubility errors would almost counteract one another. Increased reproducibility of analyses of a gas mixture was found after adoption of this uniform procedure.

Helium is slightly soluble in the carbon dioxide absorbent. If helium-carbon dioxide mixtures are being analyzed, the potassium hydroxide solution becomes saturated with respect to helium. Then if pure carbon dioxide or gas samples that are very rich in carbon dioxide are introduced, a small amount of helium will come out of solution. If sufficient time is allowed to attain a new solubility equilibrium, this effect is negligible. Otherwise, spectroscopically pure carbon dioxide will have an apparently potash-insoluble residue of about 0.15 vol. %. After several minutes this decreases to about 0.02 per cent as a new helium-solubility equilibrium is reached.

Accurate analysis of gases in much smaller volumes than those encountered in ordinary chemical work necessitated the development of a special unit.³ This unit, a modification of the design of Scholander,⁴ has been termed the "micro-Orsat."

Because of its relatively great accuracy and ease of operation, this instrument has been extensively used to analyze two-component gas mixtures whenever the available sample is too small to be handled with the conventional apparatus, that is, less than 5 ml.

3.1 Description of Apparatus. The micro-Orsat, fundamentally a Haldane analysis apparatus, consists of a buret in the male member of a four-arm stopcock whose female member has four side arms.

The four arms shown in Fig. 29.5 are attached to the female member of the buret stopcock. These arms are for (1) sample reject, (2) sample input, (3) absorption, and (4) compensation for temperature and pressure changes during absorption.

The volume of gas sample taken and the volume remaining after absorption are measured by a micrometer barrel A; the micrometer spindle B acts as a piston to raise and lower a mercury column C. The

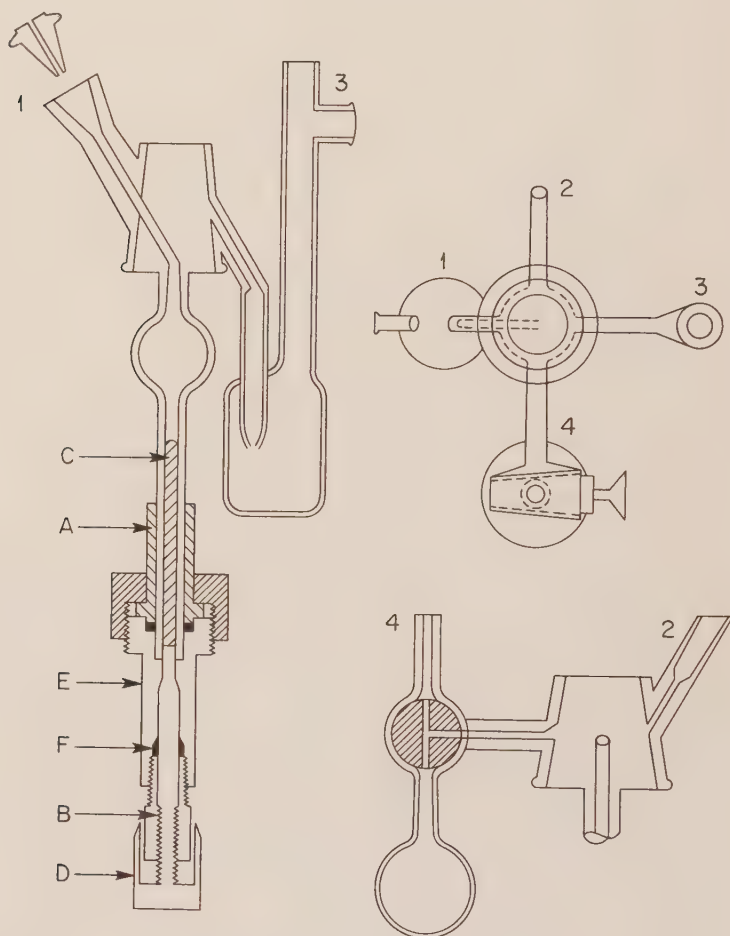


Fig. 29.5 — Micro-Orsat apparatus.

The micrometer head D is packed into a cold-rolled steel cylinder E; the spindle, sealed from the atmosphere by a leather washer F extends into the mercury reservoir.

The type of micrometer used is unimportant. Although metric graduations have been adopted up to this time, there is no reason why English graduations would not be as satisfactory.

The gas buret into which the sample is drawn consists of a glass bulb of about 0.75 ml capacity fused into the plug of the stopcock. One end of the bulb narrows to 1-mm I.D. tubing and opens in the wall of



Fig. 29.6 — Assembled micro-Orsat apparatus.

the plug. The other end, drawn into 1-mm I.D. tubing, runs coaxially down the plug as the bore of a $\frac{1}{4}$ -in. pyrex capillary and is sealed into the micrometer assembly by a stainless-steel packing gland and rubber gasket. Pressure can be exerted upon the packing by a knurled brass nut. Figure 29.6 is a photograph of a micro-Orsat apparatus assembled. Although this is not the latest model, it possesses all the essential features.

(a) Reject Arm. The exhaust gas is rejected into the atmosphere through the liquid (water for oxygen analysis, dilute sulfuric acid for carbon dioxide) of this arm, which is a 30-mm length of 5-mm I.D. tubing. Small droplets can be drawn from the liquid either to saturate the new sample or to renew the compensator drop. A trace of water is needed in the buret to assure fully water-saturated gas. Saturation by diffusion is complete within 5 sec. In an attempt to maintain a clean mercury surface, 0.25M sulfuric acid has been used instead of water but without notable success. There is, however, some advantage to an acidic reject solution when the absorbent is alkaline, as most oxygen absorbents are alkaline. If a small quantity of the absorbent is inadvertently drawn into the gas buret, it can be quickly neutralized with liquid from the reject arm. A similar accident in the case of a macro-Orsat apparatus necessitates flushing the absorbent out of the buret.

(b) Input Arm. The gas to be sampled is drawn into the buret by means of a flexible capillary waxed into the input tube. Although in earlier models this arm does not differ from the reject, in the later models it terminates in the female member of an interchangeable ground-glass joint, into the other half of which is sealed the supply tubing. This arrangement has a dual purpose; it permits rapid cleaning of the unit, and by allowing free turning of the capillary it relieves the strain on the wax seal and thus removes a source of leaks. The most commonly used supply capillary is a 10-mil I.D. by 20-mil O.D. nickel tubing 2 or 3 ft in length. Because of flushing-time considerations, material of larger diameter is not desirable.

It should be noted that the sample analyzed must be at or near atmospheric pressure if difficulties are to be avoided in the compensator arm later in the analysis.

(c) Absorption Arm. One component of the sample is quantitatively removed in the third arm of the stopcock by passing the gas back and forth between the buret and the absorption tube. This passage of the gas is caused by motion of the micrometer spindle. Each time a pass is made, the absorbent in contact with the gas is rapidly ejected through a jet into the absorbent reservoir, and mixing occurs. When only one component remains, the liquid level is returned to the starting fiduciary mark etched on the absorption arm close to its union with the stopcock.

By use of a bulb and jet arrangement for absorption the useful life of a single filling of absorbent has been increased eight times, and the mixing is much improved. The capacity of this bulb is slightly more than 20 ml. The tubing in which the actual absorption occurs is 4 cm in length and is sealed into the bulb. The jet effect occurs at the reduced end of this inner tube.

Since the life of most common reagents is at best very short, a connection is provided so that the absorption arm can be attached to an inert gas supply. After the bulb is filled, this connection must be closed. Because of the limited capacity of a bulb supply, air must be prevented from entering the open end of the bulb when the bulb contains oxygen absorbents. Two methods have been used; either (1) a small U-shaped tube filled with water is attached to the open end, or (2) a layer of oil is floated on the exposed surface of the absorbent.

(d) Compensator Arm. Because the residual gas must be measured at the initial pressure and temperature conditions, a compensator that corrects for changes during analysis has been provided. This consists essentially of a three-way stopcock connected to the buret stopcock by a 3-mm length of 0.75-mm I.D. tubing. Etched on this tubing near its joint with the buret stopcock is a fiduciary mark with which an indicating drop may be aligned. One of the two remaining arms of the three-way stopcock opens to the atmosphere; the other enters a 2-ml bulb containing 0.5 ml of either distilled water or 0.25M sulfuric acid.

A drop of liquid containing a trace of Aerosol or other wetting agent is drawn from the reject arm and carefully aligned with the fiduciary mark. Then the three-way stopcock, which has joined the atmosphere, the small bulb, and the drop, is turned so that only the latter two are connected. Thus a fixed volume of gas saturated with the bulb liquid is trapped at sampling conditions. By realigning the drop at the end of the analysis, any over-all changes in pressure or temperature, except for the thermometric mercury effect in the buret, are automatically eliminated.

As a sensitive pressure indicator the capillary drop is very satisfactory. A movement of 0.002 mm of the micrometer spindle is sufficient to cause the drop to move 0.1 mm, and, by decreasing the diameter of the tubing concerned, greater sensitivity can be obtained. The practical diameter of the tubing is, however, limited by the tendency of the liquid to stick, a tendency that can cause difficulties even in the present design. Great care must be exercised not to "blow" the drop by increasing the pressure in the micro-Orsat apparatus until it is greatly above atmospheric pressure or by cooling the compensator bulb.

3.2 Analysis. (a) Accuracy. Experimentally an over-all reproducibility of 0.04 per cent per single analysis has been obtained when operating at about 20 per cent of the absorbed component, that is, an analysis could be reported as 20.00 ± 0.04 per cent oxygen or carbon dioxide. The lower limit of error is, of course, determined by the smallest estimated division on the micrometer sleeve. If this is 1×10^{-4} cm and the diameter of the piston is 0.25 in., the smallest

measurable change of volume is 3.2×10^{-5} cc. Consequently, in a sample corresponding to a 20-mm displacement of the spindle, the maximum accuracy expected is 0.005 per cent. Actually, for other reasons the error is somewhat greater.

If the compensating bulb and gas buret remain at the same temperature, analyses are not affected by temperature changes. But if there is a variable temperature difference between the two such as might be caused by a breeze, the validity of the reported results is doubtful. If, for example, the gas contains about 50 per cent of one component, a difference of 1°C is sufficient to cause an error of 0.24 per cent in the analysis. To avoid this difficulty, the greatest single possible source of error, both water baths and thermostatted boxes have been used with partial success.

Since at the end of an analysis the gas trapped between the compensating drop and the gas buret is one component, it must be flushed several times with the next mixture to be analyzed before the actual sample is taken. If this flushing is neglected, an analysis nominally of 50 per cent may be in error by about 0.18 per cent, but a single flushing reduces the error to 0.001 per cent. A similar consideration holds for the input sections of the buret, but there the connecting tubes and supplementary equipment are of a variable volume, and no general estimate of error can be made.

Since the absorbent must be brought back to the fiduciary mark at the end of an absorption, a parallax error is possible. If the setting on the fiduciary mark is misjudged by 0.1 mm, a concentration of 50 per cent is incorrect by ± 0.008 per cent. The possible error due to parallax in the compensator is the same as in the absorption tube.

During the course of an analysis the sample, fully saturated with water vapor, is greatly reduced in volume. As a result, a part of the vapor condenses, thereby increasing the size of the liquid layer already on the mercury. Assuming a 0.25-ml residue and a 50 per cent concentration, the reported result is in error by 0.001 per cent.

Since the coefficient of volume expansion of mercury is rather large, an error of considerable magnitude is introduced into the analysis if the apparatus temperature changes after the initial sample volume has been determined. A rise of 1°C in the case of a sample requiring a 20-mm displacement of the micrometer spindle is sufficient to cause a concentration of 50 per cent to be too high by 0.013 per cent. When this is compared with the inherent instrument accuracy of 0.005 per cent, the necessity for rapid operation to minimize temperature changes is apparent.

Although most of the micro-Orsat apparatuses have given consistent analyses among themselves when checked against a standard mix-

ture, several units gave results markedly different from those obtained with the other apparatuses. The deviations in these cases were attributed to a tapered micrometer spindle and inaccurate threads.

Reproducibility of results given by the micro-Orsat apparatus is somewhat greater than that of the conventional macro instrument, and there is a Gaussian error distribution. An extensive study of the reproducibility was made by determining the concentration of oxygen in room air, using three different operators and two micro-Orsats with a random interchange of instruments and observers. These data are tabulated in Table 29.1.

(b) Reagents. The reagent chosen, as in all such analysis units, must quantitatively absorb one of the components and leave the other

Table 29.1 — Reproducibility of Micro-Orsat Analyses for the Oxygen Content of Air

Micro-Orsat No. 1			Micro-Orsat No. 2		
Operator	Oxygen, %	Av. deviation	Operator	Oxygen, %	Av. deviation
1	20.702	0.150	3	20.851	0.013
1	20.950	0.098	3	20.969	0.105
2	20.854	0.002	3	20.825	0.039
2	20.936	0.084	3	20.797	0.067
3	20.820	0.032	2	20.894	0.030
			1	20.850	0.014
Average	20.852	0.073	Average	20.864	0.045

unaffected. The 30 per cent solution of potassium hydroxide commonly used with conventional Orsat apparatuses removes carbon dioxide satisfactorily.

Several reagents were tried for air and oxygen-nitrogen mixtures. Pyrogallol, a common analytical absorbent for oxygen, and Ox-sorbent, a commercial preparation, were found to have too short a life to be practical. In fact, the Ox-sorbent would react with only four times its volume of oxygen; this necessitated frequent refilling. A modified pyrogallol preparation, Seez-O₂, has been employed exclusively. It is claimed that this reagent absorbs 20 times its own volume of oxygen and, to some extent, regenerates itself after use. Because of this great capacity it is unnecessary to flush the micro-Orsat with inert gas when filling the absorption bulb.

(c) Procedure. At the completion of an analysis the gas residue is exhausted through the reject tube, the mercury column being driven in the arm as far as possible to assure the expulsion of all gas bubbles. At this time the atmosphere, compensator bulb, and indicating droplet are connected through the three-way stopcock.

The unit is turned so that the gas buret and input arm are connected, and a 10-mm sample, as read on the micrometer, is drawn into the buret. This is the first flushing sample, and it is used as indicated above to prevent errors resulting from leaving one component of the gas mixture in the supply capillary and compensating arm. The Orsat is turned to the compensator, and the indicating drop is moved vigorously back and forth to ensure adequate mixing. Then the drop is drawn as far toward the buret end of the capillary as possible, and the unit is turned so that the gas may be rejected into the atmosphere.

Another 10-mm sample is drawn, and the above step is repeated.

With the buret connected to the reject arm, enough liquid is drawn in to give a convenient zero point. If sufficient liquid is not present to saturate the gas to be analyzed, vapor pressure effects may occur when the sample is forced into the absorbent. This value, recorded as the zero point, only rarely coincides with the zero of the micrometer.

The sample is drawn through the input arm. This is usually about twice the size of the flush sample, but in no case may it exceed 20 mm on the micrometer, since below this level the spindle is pulled out of the leather packing and air may enter the apparatus. Care must be taken to obtain gas at or near atmospheric pressure; a Toepler pump is convenient for this purpose.

The compensator arm and buret are connected, and the droplet is drawn to the fiduciary mark. The three-way stopcock is turned so that only the buret and compensating bulb are connected. After 30 sec the indicating drop is readjusted if necessary, and the micrometer reading is recorded as the volume of the sample.

The sample is driven into the absorbent by rotation of the stopcock. After 1 min the gas is drawn into the buret and then returned to the reagent. This process is repeated until absorption is complete as indicated by a micrometer reading constant to within ± 0.002 mm. The absorbent is drawn carefully to the fiduciary mark on the neck of the absorption tube.

Thirty seconds after the compensator bulb has been connected with the buret, the drop is reset at the fiduciary mark. The corresponding micrometer reading indicates the volume of the residue.

To avoid the use of the fiduciary drop as an aid in flushing a gas sample out of the apparatus, a modified procedure is occasionally used. On completion of analysis the droplet is drawn from the reject arm and forced into the compensator capillary to form a new drop; the excess liquid is returned to the reject. Only enough gas is taken in to reset the drop and determine the zero point. The subsequent procedure is that starting with the step where the sample is drawn

through the input arm. Regardless of the procedure adopted the supply capillary must be carefully flushed between samples of different composition.

The micro-Orsat is the most accurate and the easiest to operate of the various two-component absorption-analysis units used. It is relatively cheap and simple, and by merely changing absorbents it can be used for a great many binary mixtures. Where only small samples are available it is invaluable, and in addition it has certain advantages of precision regardless of the size of the sample.

4. THERMAL CONDUCTIVITY^{5,15}

The rate of heat conduction through a gas under given conditions is a consistent, measurable property of that gas. The conductivity of a given mixture of two gases usually has a unique value somewhere between the conductivities of the two constituent pure gases. A few gas pairs exhibit a conductivity maximum. The conductivity of the mixture can be predicted from theoretical considerations. In practice the characteristics of the particular apparatus as well as the heat conductivity of the gas are such that each apparatus must be calibrated for the particular gas or mixtures of gases to be used. The method depends on measurement of the rate of heat flow through the gas by determination of the electrical resistance of a hot wire immersed in the gas.

“Thermal conductivity” refers to a coefficient defined by the relation

$$Q = KA \frac{dT}{dr}$$

where Q is the quantity of heat flowing per second from a surface of area A , (dT/dr) is the temperature gradient, and K is the coefficient of thermal conductivity for the gas being considered. The coefficient is expressed as calories per centimeter per second per degree centigrade.

A suitable pair of gases should have a large difference in molecular weight and should be noncorrosive. The first of these criteria is to ensure a large difference in thermal conductivity and therefore a greater accuracy. The reason for the second is obvious, but cells and filaments have been developed for use with corrosive gases. The gases of a pair such as helium-carbon dioxide have a greater difference in conductivity than a pair such as carbon dioxide-nitrogen, which have more nearly equal molecular weights. Therefore greater

experimental precision is required to obtain the same degree of accuracy for a mixture of gases having almost equal molecular weights.

4.1 Description of Apparatus. The apparatus consists of a Wheatstone bridge supplied with a known constant current from an external source. Two arms of the bridge are fixed, equal resistances. The other two arms consist of two matched resistances mounted inside two gastight cylindrical chambers, coaxially with the chambers. The current through the bridge divides equally to the two resistances. If the two chambers are filled with gases having equal heat conductivities, the heat is conducted at the same rate from each filament to the walls of its respective container. Then the temperatures, and hence the resistance, of the two filaments will be equal, and the bridge will be balanced. But if the chambers are filled with gases having different heat conductivities, the two wires will lose heat at different rates. Then the temperatures and the resistances will be different, and the bridge will be unbalanced. The amount of unbalance, which is proportional to the difference in conductivity of the two gases, can be measured in the usual way, by a high-resistance potential meter across the bridge.

One of the cells, called the "reference cell," of a calibrated unit is usually filled with a standard gas and then sealed. Gases to be analyzed are passed through the other cell, which is called the "sample cell."

Several types of thermal-conductivity gas analyzers have been used: General Electric gas analyzer, Leeds & Northrup thermal-conductivity bridge, modified Princeton-type gas analyzer, and Engelhard double by-pass thermal-conductivity unit.

(a) General Electric Gas Analyzer.⁶ The reference and sample cells are mounted in the same metal block. Any changes in ambient temperature will affect both cells proportionally, provided that the gas being analyzed does not differ greatly in composition from the reference gas. Thus bridge output will be independent of ambient temperatures over the normal room-temperature range.

In the actual gas-analyzer unit, readings are taken with a static pressure in the cell, prior to which the cell has been thoroughly flushed by allowing the unknown gas mixture to flow through it for approximately 1 min.

A photoelectric amplifier is employed, enabling the use of a 5-ma recording ammeter as the indicating instrument. This amplifier, which is a self-balancing potentiometer, has a linear characteristic. Amplification is not affected by gradual aging of the tubes, or by variation of tube constants or of the light source.

(b) Modified Princeton-type Gas Analyzer.⁷⁻¹⁰ Although the General Electric thermal-conductivity unit was considered in many cases

to be a suitable instrument both from the viewpoint of stability and accuracy, this instrument was not generally available at one time. It was therefore necessary to construct individual cell units in the laboratories where it was desired to analyze gas mixtures by thermal conductivity.

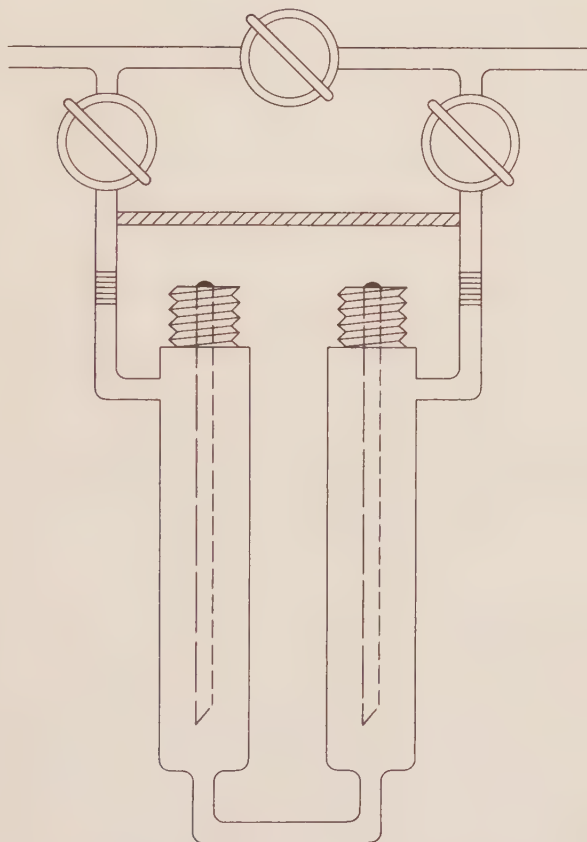


Fig. 29.7—Thermal-conductivity cells constructed from Mazda lamps.

The gas cells were constructed from carefully selected Mazda lamps, T-6½, 25 watts, 110 volts. General Electric T-10 25-watt lamps have also been used. The filaments should be fairly taut. A piece of soft-glass tubing is sealed on both the top and bottom of the lamp as shown in Fig. 29.7.

The cells are conditioned⁸ before actual use by reducing the oxide on the filaments by a stream of hydrogen and by outgassing the fila-

ments while the proper heater current is applied. The process consists in pumping the cells under high vacuum, filling with hydrogen, reducing for 15 min, and pumping. Rehydrogenation is repeated several times and is followed by a prolonged pumping for about 24 hr at a pressure of about 25μ Hg. Care must be taken not to admit air into the bulbs while the filaments are heated. Finally the cells are filled with carbon dioxide at atmospheric pressure.

It is necessary to find two pairs of cells of resistance differing by less than 1 per cent. These four cells are then connected together

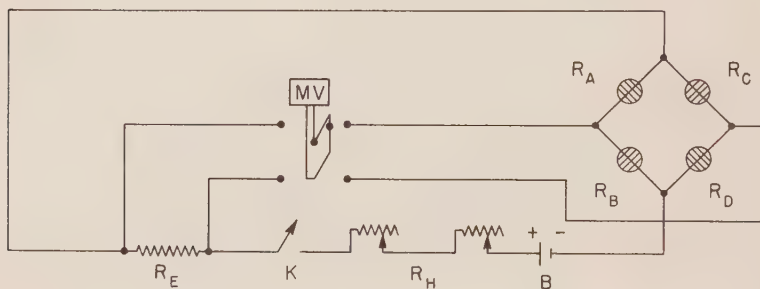


Fig. 29.8—Thermal-conductivity bridge. R_E is a shunt resistance to permit the use of the millivoltmeter (MV) as a milliammeter. R_H is the rheostat to regulate the heater current. B is a 6-volt storage battery.

to form the four arms of the bridge. If A and B represent one pair of similar cells and C and D the other pair, then A and C should be connected so that the gas mixture for analysis flows through them and B and D are connected for the standard gas. The four filaments are connected together electrically in the same order. This arrangement of the cells, Fig. 29.8, increases the sensitivity of the bridge, since the off-balance is a function of the difference of the product of resistances (R_B) (R_D) and (R_A) (R_C).

If the cells are nearly enough alike, the effects of ambient temperature changes on the bridge are negligible. Immersion of the cells in an oil-filled thermostat gives very good temperature control. The temperature effect is also minimized by the use of four similar cell resistances instead of three standard wire-wound resistances and one cell.

(c) Engelhard Double By-pass Thermal-conductivity Unit.¹¹ The platinum filaments inside the measuring chambers are surrounded by protective sheaths of thin-walled quartz tubing. The main flow of gas passes through nearby tubes parallel to the measuring cells;

these tubes are connected at each end to the measuring cells, hence the designation of "by-pass-type" cells. This is advantageous since a large range of flows may be used, but it is a disadvantage in that the time required for flushing one gas out of the cell by the next is increased.

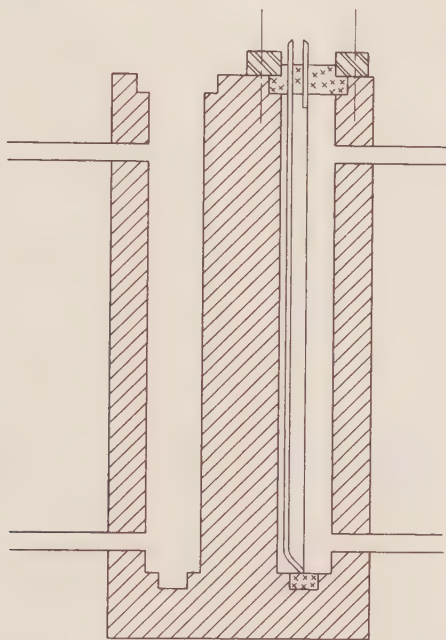


Fig. 29.9—Thermal-conductivity cell block for corrosive gases.

(d) Thermal-conductivity Unit for the Analysis of Nitrogen-Corrosive Gas Mixture.¹² A thermal-conductance cell was designed and built in a Duralumin block. In each of the tubular openings in the block a platinum wire was mounted and supported in a stirrup. The copper leads from the platinum filaments were electrically insulated from the surrounding metal by plastic bushings and were sealed vacuum-tight with Apiezon wax. The use of Apiezon prevented the use of temperatures much above room temperature.

(e) Analysis of Hydrogen Fluoride.^{13,14} A continuous automatic recording unit for analysis of hydrogen fluoride in the three-component flowing system [nitrogen (0 to 100 mole %)-oxygen (0 to 100 mole %)-hydrogen fluoride (0 to 10 mole %)] was constructed. The gas stream passes through one arm of a specially designed thermal-conductance cell (Fig. 29.9), through a sodium fluoride trap to remove hydrogen

fluoride, and finally through the second arm of the thermal-conductance cell. The measured potential is essentially determined by the difference in thermal conductance of the gases in the two cell arms. This differential method makes it independent of variations in oxygen and nitrogen content and minimizes fluctuations in flow, pressure, and ambient temperature.

The method is accurate to 0.1 mole % of hydrogen fluoride.

The thermal-conductance cells are holes drilled in a solid monel block. In each hole is fitted a stirrup to support a 2-mil platinum wire which is spot-welded at each end to the stirrup. The stirrup is centered in the hole by plastic collars at each end. Plastic disks also serve as gaskets to maintain a vacuum seal and to insulate the leads to the filaments. These disks are clamped in place by brass collars and screws. The plastic is a solid polymer, $(C_2F_3Cl)_n$, which permits pretreatment of the cell with fluorine.

An alternative method¹⁴ for an oxygen-nitrogen-hydrogen fluoride system involves the conversion of the hydrogen fluoride to hydrogen and the measurement of the thermal conductance of a nitrogen-hydrogen gas mixture. Hydrogen fluoride is removed by condensation with liquid nitrogen. The thermal conductance of the oxygen-nitrogen mixture is determined; then the oxygen is removed by reaction with copper at 600°C.

Hydrogen fluoride can be converted to hydrogen by two methods: reaction between hydrogen fluoride and copper oxide in a copper reactor to form water, followed by a conversion of the water to hydrogen in an aluminum reactor, or by direct reaction between hydrogen fluoride and aluminum to form hydrogen and aluminum fluoride. Both these reactions go to completion at a temperature of 800°C in the aluminum reactor.

The thermal conductance of the resultant hydrogen-nitrogen mixture is measured. Its thermal conductance minus the zero readings for the oxygen-nitrogen mixture is compared with a calibration curve.

$$\text{Mole \% HF in gas stream} = \frac{(\text{mole \% HF in N}_2)(100)}{(\text{mole \% O}_2 \text{ in N}_2) \frac{100 - \text{mole \% HF in N}_2}{100 - \text{mole \% O}_2 \text{ in N}_2} + 100}$$

4.2 General Characteristics of Thermal-conductivity Apparatus.
(a) Pressure Dependence of the Cells. Since the heat conduction of the gas mixture varies with the pressure, it is essential that the pressures be accurately regulated, especially below 10 cm Hg. The pressure vs. bridge-output curve is quite steep below 10 cm Hg in most cases. This pressure effect for helium is illustrated in Fig. 29.10.

For carbon dioxide the dependence down to 8 cm Hg is small and practically linear. For helium and hydrogen the pressure dependence is somewhat greater and not quite linear down to 15 cm Hg.

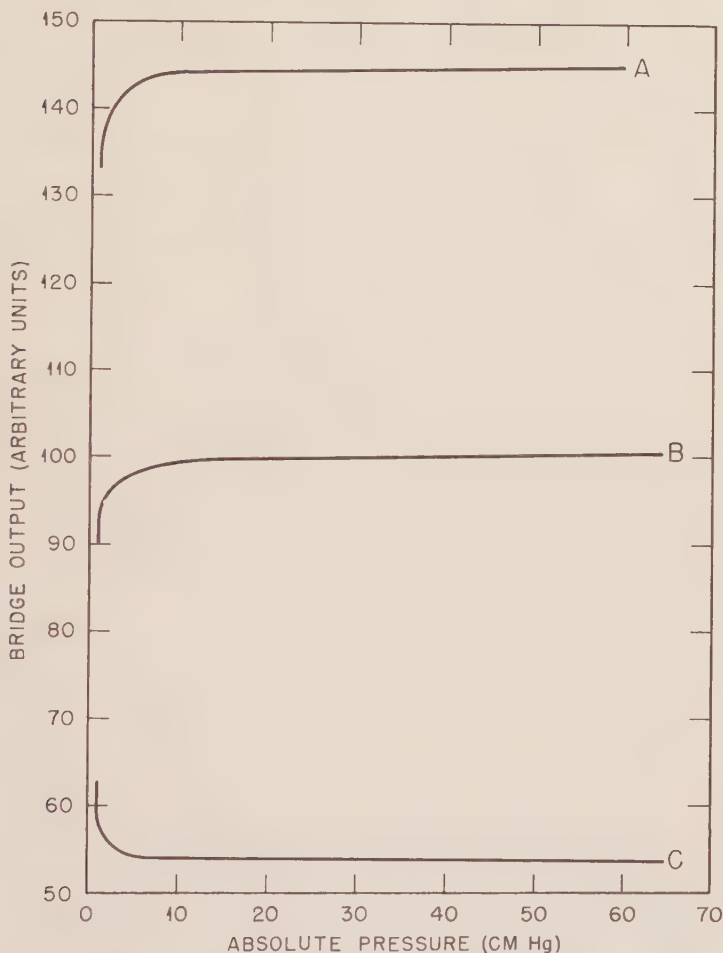


Fig. 29.10—Pressure dependence of thermal conductivity. Curve A, 100 per cent helium, 20 ml per minute. Curve B, 40 per cent carbon dioxide–60 per cent helium, static. Curve C, 100 per cent carbon dioxide, 30 ml per minute.

Any variation from the pressure at which the unit was calibrated will cause an appreciable deviation from the actual gas composition. Pressure variations can be eliminated by use of siphon bellows as pressure regulators in the gas inlet line.

(b) Effect of Gas Flow Rate. With gas flows between 20 and 1,000 ml per minute at atmospheric pressure, the current reading is not more than 1 per cent different from the static reading for helium and helium-carbon dioxide mixtures, and is about 2 per cent for pure carbon dioxide. The cells may also be calibrated for static analysis. The cell is flushed with the gas to be analyzed and then closed off by stopcocks. In most cases it is more convenient to use the continuous-flow method.

It is possible that small differences in absolute readings between flow and static samples may be due to the flow coefficient of thermal conductance.¹²

(c) Effect of Gas Temperature. A change of 100°C in the temperature of the entering gas results in approximately 1 per cent change in the bridge output.

(d) Flushing Time. For small changes in gas composition (10 per cent in either component in helium-carbon dioxide mixtures, for example) if one mixture in the cell could be instantly replaced by the other, the unit would come to the new equilibrium in less than 2 min. In normal operation, however, it is not possible to replace instantly one gas by another, and a period of time is required to flush out one gas mixture and to fill the cell with the next. This time depends on the cell geometry, the rate of flow, the physical properties of the two gases, and the amount of inlet tubing.

(e) Errors. There are two chief sources of error in thermal-conductivity methods of gas analysis: inability to set the heater current exactly at the predetermined value and inaccuracy in reading the output voltage. The probable error from both these sources is reduced as more accurate control and measuring instruments are used. There is a practical limit, however, beyond which it is not feasible to improve the measuring instruments.

Another error may be introduced during calibration of the unit by the presence of impurities in the calibrating gas mixtures. Appreciable amounts of nitrogen and oxygen have been found in commercially prepared helium-carbon dioxide mixtures. After absorbing the carbon dioxide in potassium hydroxide solution and the oxygen in alkaline pyrogallol, the residual nitrogen-helium mixture can be analyzed by thermal conductivity. Calibration curves for these nitrogen-helium mixtures can be prepared from spectroscopically pure gases.

5. INTERFERENTIAL ANALYSIS¹⁶

5.1 Principle. Gas mixtures may be analyzed by the measurement of their refractive indices by interferometric methods. The method is applicable only to gas pairs in which the two components have rel-

atively large differences in refractive index. The method has been applied to binary mixtures such as acetylene and dimethyl ether.¹⁶ Any impurities in the mixture change the refraction, so it is necessary that the system contain only the two components.

5.2 Apparatus and Procedure. A Jamin interferometer was employed in the measurement of the refractive indices of the mixtures. This instrument produces interferences by division of amplitude. If a phase difference is introduced between the two light paths by filling one tube of length L with a gas of refractive index n while the other tube is evacuated, the fringe pattern will shift by an amount corresponding to the optical path difference, $m = (n - 1)L$. The refractive index at standard temperature and pressure may be calculated from the relation

$$(n - 1)_{\text{STP}} = \left(\frac{m\lambda_{\text{vac}}}{L} \right) \left(\frac{760}{P} \right) \left(\frac{T}{273} \right)$$

where m = the number of fringes counted

λ_{vac} = the wavelength in vacuum of light employed

L = the length of the gas tube

P = the final pressure

T = the absolute temperature of measurement

Measurements were made with the sodium D line, 5893 Å. The small pressures were measured by means of a cathetometer. Although the interferential method of analysis cannot be applied to static systems, it does lend itself to flow systems if the gas mixture is passed through the interferometer tube.

6. MAGNETIC SUSCEPTIBILITY^{17,18}

Oxygen has a paramagnetic susceptibility of 106×10^{-6} e.m.u. per gram. Nitrogen and all other atmospheric gases have diamagnetic susceptibilities of about 0.3×10^{-6} e.m.u. per gram. Therefore the concentration of oxygen in atmospheric gases can be determined by measurement of the magnetic susceptibility of the gas sample.

7. DETERMINATION OF THE MOISTURE CONTENT OF GASES

The most important factor in the determination of the moisture content of gases is the time involved for a determination. Several dew-point indicators were developed to give this information in a conveniently short time.

7.1 Dew-point Indicator Method.¹⁹ (a) Principle. A polished copper tube in a gas stream is caused to assume an unchanging but non-

linear temperature gradient. At some point along the tube a frost line will form. The temperature at that point can be determined by means of thermocouples spaced along the length of the copper tube.

(b) Accuracy. The precision of an individual measurement is about $\pm 1^\circ\text{C}$ down to a dew point of -70°C ; below this temperature there is difficulty in observing the ice crystals, which are exceedingly small and which form very slowly.

Experimentally the apparent dew point varies with the rate of gas flow and approaches the true value from below as the flow approaches zero. The thermocouples read an average temperature on the gradient in the wall perpendicular to the surface of the copper tube. For most applications this error is negligible at flows of 100 to 200 ml per minute or lower.

(c) Apparatus. The apparatus is shown in Fig. 29.11. The temperature gradient is maintained by allowing the incoming gas to strike one end of the copper tube and by cooling the other end in liquid air or nitrogen. Thus heat flows along the tube from the gas stream to the cooling liquid. At a constant level of refrigerant and a constant flow of gas the temperature gradient is constant.

(d) Procedure. The copper is cooled slowly by gradually raising the liquid-air level until a frost line is observed moving up the tube; then a constant temperature is maintained for 5 to 10 min in order to permit the establishment of a steady state. When the frost line comes to rest, the temperature is estimated at the frost line by reading the thermocouples, and an interpolation is made between the thermocouples. The temperature difference between the thermocouples depends on the rate of gas flow, but with the design shown in Fig. 29.11 it is about 2 to 3°C at gas flows of 100 to 200 ml per minute.

It should be noted that the frost line is not always sharp; the ice forms on the tube in isolated crystals, not in a continuous haze. The size and spacing of the crystals depend on the rate of gas flow, the water content, and the extent to which the rod is cooled below the dew point; but in general the crystals become smaller and sparser as the frost line is approached. The line is taken as the level above which no crystals are seen. A good light and a magnifying glass are needed to determine this level with certainty.

If true equilibrium is not attained and if the temperature of the surface is not really measured, the apparent dew points will be too low. Equilibrium can be checked by making the frost line move up or down with a slight decrease or increase in the average temperature of the rod. If the rate of cooling is kept reasonably low and the temperature is held constant for 5 to 10 min, equilibrium will be established for all practical purposes.

7.2 Determination by Thermometric Measurement of the Heat of Reaction with Dehydrating Agent.²⁰ (a) Principle. If a moist gas is passed over a dehydrating agent, sufficient heat is liberated to permit measurement of the temperature increase by means of a thermopile.

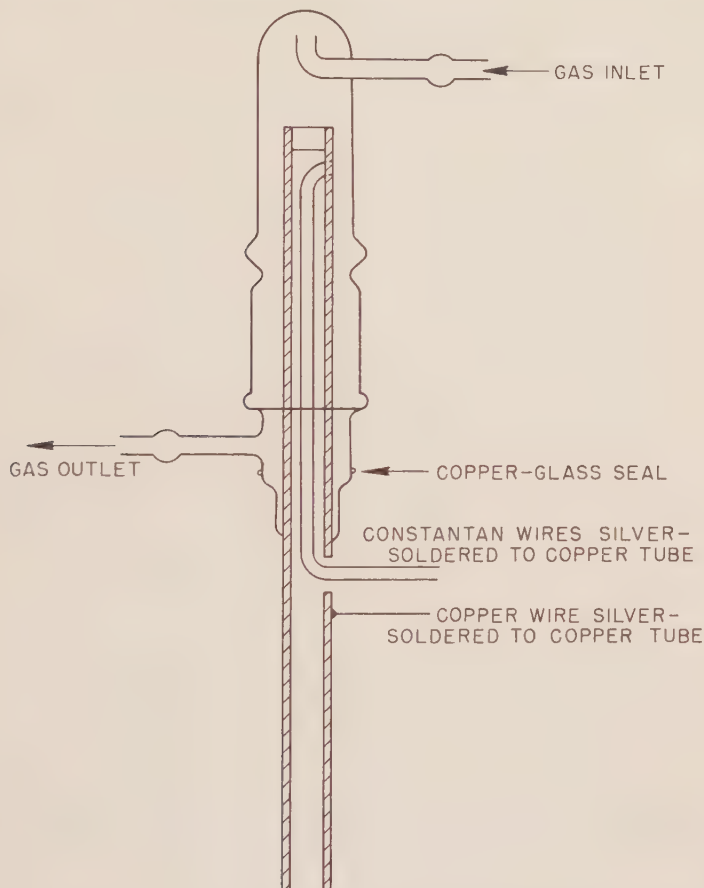


Fig. 29.11 — Dew-point indicator.

(b) Apparatus and Reagents. The thermopile cell may be constructed of either metal or plastic. It contains the dehydrating agent and the thermopile.

Various dehydrating agents could be used: magnesium perchlorate (Anhydron), calcium chloride, or phosphorus pentoxide. Anhydron was found to be the most satisfactory. It can be handled easily, is

readily obtainable, is inert to a large number of gases, and has a high heat of solution, 25 kcal per mole. The vapor pressure of water above Anhydrone is less than 0.001 mm Hg. Anhydrone retains its high drying efficiency for a long time.

(c) Procedure. The gas stream is passed through the thermopile cell, and the temperature is recorded. A constant and relatively low rate of gas flow is maintained.

Temperature readings are reproducible. The procedure is very satisfactory for moisture contents of less than 1.5 mg of water per liter.

Table 29.2—Dew-point Determination with Cobalt(II) Cyanide

Paper temperature, °F	Dew-point range, °F	Color
+33	-13 and above	Tan
	Below -22	Tan to light purple (transition)
	Below -27	Light purple
	Below -31	Medium purple
	Below -37	Purple
+79	+33 and above	Tan
	Below +20	Tan to light purple (transition)
	Below +12	Light purple
	Below -6	Light purple to medium purple
	-6 to -22	Gradual darkening from medium purple to purple
	Below -22	Purple
+122	Approx. +60	Tan to light purple (transition)
	Below +50	Light purple
	Below +23	Medium purple
	Below +5	Purple

7.3 Determination with Cobaltous Cyanide Paper in Inert Gases.^{21,22}

(a) Principle. The color of completely hydrated cobalt(II) cyanide is tan; loss of water of hydration results in a gradual change to a purple color.

(b) Reagent. Cobalt(II) cyanide, Co(CN)_2 , is deposited from aqueous solution containing bivalent cobalt on the addition of cyanide. It is brown to tan in color and is deposited as a hydrate. The precipitate is soluble in excess potassium cyanide, yielding potassium cobaltocyanide, $\text{K}_4\text{Co(CN)}_6$, which is so powerful a reducing agent that it liberates hydrogen from aqueous solutions. Hence an excess of cyanide ion is to be avoided, and in practice it is found that the most stable precipitates are formed when a 15 per cent excess of cobalt is used and when the cyanide is added to the cobalt.

If the precipitated and dried cobaltous cyanide is heated in air to 100°C, it turns purple. This color change is completely and rapidly reversible when the cobaltous cyanide is cooled. At 200°C the compound is a true blue and decomposes to the oxide at 250°C. It is believed that the blue cobaltous cyanide is still partly hydrated.

A thin slurry of the very insoluble $\text{Co(CN)}_2 \cdot 3\text{H}_2\text{O}$ is prepared by the drop-by-drop addition of 4.4 ml of 0.146M potassium cyanide to 4.0 ml of 0.93M cobalt(II) acetate. The precipitate is digested for 3 min and then filtered in the following way: A Whatman No. 42 12.5-cm filter paper is wet with water and spread over the plate of a coarse-fritted

Table 29.3—Trichloroethylene in the Atmosphere

Amt. by volume, ppm	Flame Colors		
	Inside cone	Outside cone	Tip of flame
Less than 75	"Hot" blue	"Hot" blue	"Hot" blue
100 to 200	"Hot" blue	"Hot" blue	Green
300 to 500	Green	Green	Aquamarine
600 to 800	Aquamarine	Aquamarine	Aquamarine
900 to 1,000	Aquamarine	Aquamarine	Purple
1,500 to 2,000	Aquamarine	Purple	Orange
2,000 and over	Aquamarine*	Purple*	Orange

*At 2,000 ppm and above smoke is produced in addition to the flame colors.

glass filtering funnel 9.7 cm in diameter. The entire precipitate is stirred up and deposited immediately on the paper while applying suction. A uniform deposit is obtained in this way. It is washed several times with distilled water, then sucked dry with the aspirator, and dried at 110°C in an oven. After drying the paper is cut into 0.6- by 5-cm strips. Paper prepared as above contains about 0.5 mg of cobalt(II) cyanide per square centimeter of paper area on one face only.

(c) Procedure. The gas to be analyzed is passed over or through the paper saturated with cobalt(II) cyanide. The color produced is partly dependent on the indicator-paper temperature; this dependence is shown in Table 29.2.

8. MISCELLANEOUS ANALYSES

8.1 Determination of Mercury Vapor in the Atmosphere.²³ The air to be sampled is drawn through an iodine-potassium iodide solution by means of a Midget impinger. The sample is analyzed for mercury by a modification of the method of Polejaeff.²⁴

The mercury forms the red-yellow mercuric iodide. A suspension of white cuprous iodide is then formed in the same solution by the addition of cupric sulfate and sodium sulfite. The cuprous iodide and mercuric iodide react to form the dark-red, slightly soluble Cu_2HgI_4 . The sample is compared with a series of freshly prepared standards.

8.2 Determination of Trichloroethylene in the Atmosphere.²⁵ The concentration of trichloroethylene in the atmosphere can be semi-quantitatively evaluated by the flame color produced by the Imperial Halide Gas Leak Detector. The flame color is due to volatile copper halides. The colors obtained are shown in Table 29.3.

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Part C

MASS SPECTROSCOPY

By L. L. Quill

The mass spectrometer¹ as an instrument for the analysis of the gas ions made by electron impact has been greatly improved in accuracy and convenience in recent years. Commercial models of the instrument have been developed and have proved to be very useful in oil and rubber industries for the analysis of hydrocarbons. In comparison with the analysis of gas ions very little use has been made of the analysis of the ions of solid samples produced by the vacuum spark. This source, combined with a double-focusing mass spectrograph, was developed in 1934 and has proved very useful in physics in the study of the isotopes of many elements. An outstanding feature of this source which gives it a unique advantage for analytical purposes is that it has no blind spots and will show every element that may be present in a sample.

The mass spectrograph may be used for the isotopic analysis of water,²⁻⁴ uranium,⁵ and stable isotopes.⁶ It may also be used for the qualitative analysis of gaseous mixtures and quantitative analysis of uranium,¹ plutonium, fluorocarbons,⁸ and other substances.¹ The instruments used have been described by various workers (see references 3, 6, 7, and 9).

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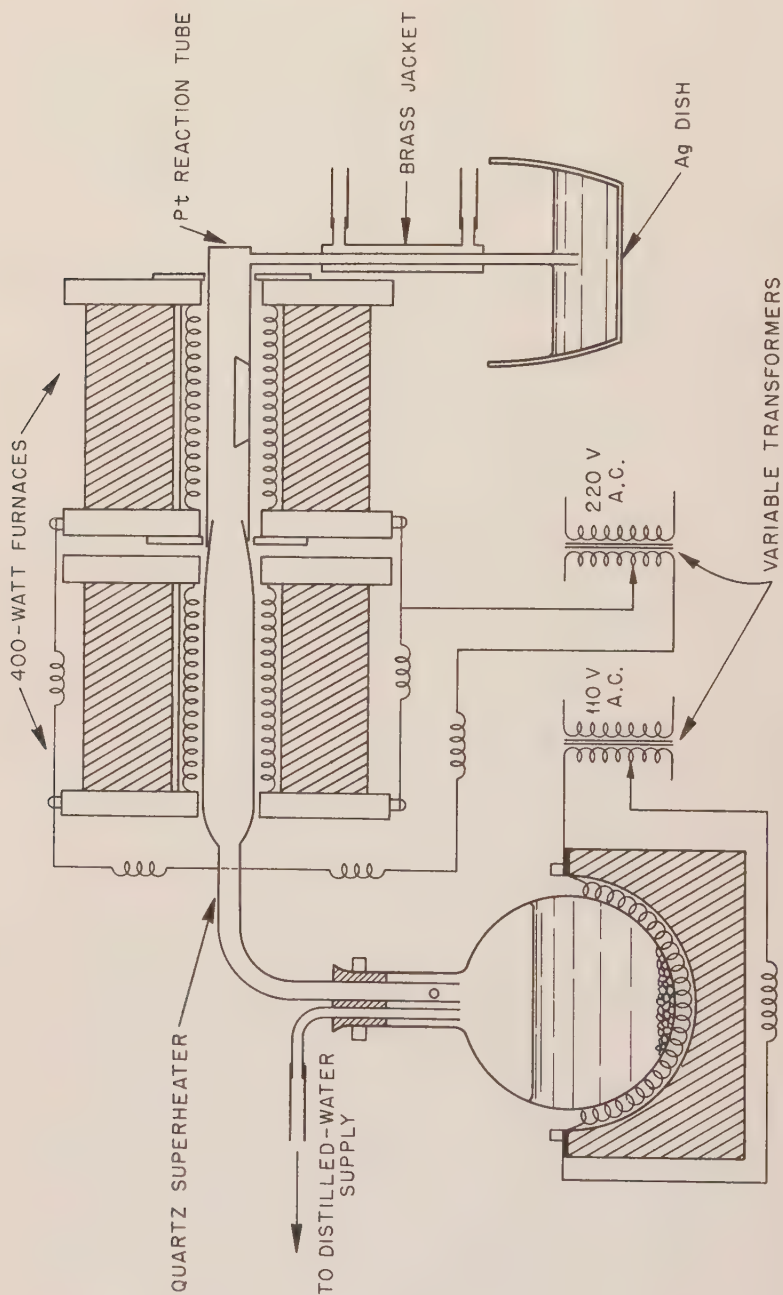


Fig. 29.12—Pyrohydrolysis apparatus.

Part D

PYROHYDROLYSIS

By J. C. Warf

The analysis of many hydrolyzable halides is often accomplished rapidly and accurately by a pyrohydrolytic method. The salt is introduced into a reaction tube and heated while being exposed to a current of superheated steam. The steam carries out the volatile acidic component, which is condensed and titrated with a standard base. The oxide remaining in the reaction tube is weighed. Temperatures ranging from 300 to 1000°C are employed; the latter temperature is most common.

The apparatus for fluorides, as shown in Fig. 29.12, consists of a platinum reaction tube about 150 mm long and 20 mm in diameter which is attached by a tapered joint to a quartz preheater as shown. Both are heated electrically by hinged-top furnaces. The quartz preheater may be eliminated by the use of a single, long, platinum reaction tube. The exit of the platinum tube is gold-soldered to a platinum condenser, and a silver or platinum dish is provided to catch the condensate.

When the halide is a fluoride, a platinum reaction tube is necessary; it may be used with chlorides and bromides as well. Quartz or glass may be used for the chlorides and bromides. Pyrohydrolytic analysis of iodides has not proved practical. The technique is primarily adapted to the analysis of easily hydrolyzed fluorides such as UF_4 , ThF_4 , AlF_3 , BiF_3 , MgF_2 , ZnF_2 , and rare-earth fluorides, although it is equally satisfactory for chlorides such as UCl_4 , UCl_3 , ZnCl_2 , MgCl_2 , and rare-earth chlorides. Beryllium fluoride is hydrolyzed only slowly at 1000°C. Complete analyses can be run in 30 min in most cases. Errors are usually less than 0.05 per cent. The procedure has been adapted to micro work.

It has been found that difficultly hydrolyzed fluorides, such as LiF , NaF , CaF_2 , and BaF_2 , and chlorides, such as LiCl , NaCl , CaCl_2 , and BaCl_2 , may be pyrohydrolyzed rapidly if first mixed with an excess of U_3O_8 . During the reaction a diuranate of the metal is probably formed, permitting the halogen to be completely expelled. Certain other oxides, such as Al_2O_3 , Cr_2O_3 , and V_2O_5 , also act as pyrohydrolytic accelerators. Fluoro salts, such as Na_2SiF_6 , K_2CbF_7 , and

Na_2BeF_4 , are rapidly hydrolyzed at 1000°C after being mixed with U_3O_8 .

The apparatus is useful for converting fluorides to oxides for spectrographic work, for example, when beryllium fluoride is to be analyzed for aluminum and the available spectrochemical calibration curves are based on beryllia. Steam at 600 to 900°C smoothly converts metals such as uranium, thorium, iron, and beryllium to their oxides. This is especially useful in the cases of thorium and beryllium metals, because air ignition of thorium gives a coarse dense oxide and beryllium is resistant to air oxidation.

9. ANALYSIS OF FLUORIDES

Procedure. The temperature of the reaction tube is brought to 1000°C , and the apparatus is steamed out. A small amount of water is collected in the dish so that the condenser tip is covered. A sample of UF_4 , ThF_4 , or some other hydrolyzable fluoride containing about 75 mg of fluorine is weighed into a platinum boat, and this is introduced into the middle of the reaction tube. Care is taken that the reaction tube is snugly fitted on the quartz preheater. The steam rate is adjusted to 2 to 3 g per minute. Usually about 5 min is required for complete hydrolysis, and the steam is passed through a few minutes after the distillate is no longer acid. The distillate is then titrated with 0.1N sodium hydroxide, using phenolphthalein indicator. The boat is withdrawn, ignited, cooled, and weighed, which gives the amount of U_3O_8 , ThO_2 , or other oxide.

10. FLUORIDES OF LIGHT METALS

Procedure. The proper amount of material to be analyzed (BeF_2 , CaF_2 , K_2ThF_6 , etc.) is weighed into a small glazed evaporating dish, and 0.3 to 0.5 g of pure U_3O_8 is added. The mixture is ground and mixed well with a small pestle, and when homogeneous it is tapped into the platinum boat. The dish is swept out using a little U_3O_8 . The mixture is pyrohydrolyzed at 1000°C , as in the case of UF_4 , until no more HF is evolved, and the acid is titrated.

11. ANALYSIS OF UCl_4 , UCl_3 , UBr_4 , AND UBr_3

Procedure. The procedure for these halides is the same as that for fluorides with the following modifications: Sample sizes are chosen so that the total amount of 0.1N sodium hydroxide required to titrate the HCl or HBr will be 30 to 40 ml; the halides are weighed in tightly covered weighing bottles and transferred to the boats in a dry box, and the weighing bottles are again weighed; the boats are in-

serted as quickly as possible into the reaction tube. However, in most work the transfer of the halide from the weighing bottle to the boat may be done in air rather than the dry box without serious error. Either quartz or platinum may be used for the pyrohydrolytic reaction tube. It is brought to about 500°C before the sample is inserted, and the temperature is gradually raised to 1000°C. The residual oxide in the boat is weighed.

Part E

X-RAY ANALYSIS

By L. L. Quill

Three types of analyses utilizing x rays may be used in the determination of unknown samples. The first method is the diffraction of a beam of x rays by a crystal of the substance, followed by an interpretation of the resulting crystal-structure diagram. The second method, designated as "x-ray spectroscopy," consists in producing the characteristic x radiation of the sample and in analyzing the resultant spectrum. A third method, dependent upon the absorption of x rays, has been used for the determination of uranium.

12. X-RAY DIFFRACTION

The x-ray diffraction method of analysis¹ is based on this fact: When a source of monochromatic x rays is passed through a crystalline substance, in the form of a single crystal or powder, the same substance always gives the same pattern, and in a mixture of substances each produces its pattern independently of the other. Considerable use has been made of this method, and Hanawalt et al.² have given a classification system for use in analysis which is recommended by the American Society for Testing Materials.³ Its chief use on the Project was the determination of lattice constants and the nature of the different compounds of uranium,^{4,5} plutonium,^{4,6,7} and other Project materials.⁷⁻⁹

13. X-RAY SPECTROSCOPY

In x-ray spectroscopy the sample is made the target of the x-ray tube. The resultant x rays are reflected from a crystal to obtain the

x-ray spectrum, which is recorded on a photographic film or plate. The essential apparatus consists of easily demountable x-ray tubes, a spectrograph with a crystal, pumps to evacuate the system, high-tension equipment, and plate-measuring devices. Standard reference works describe not only the apparatus but also the difficulties involved in the analytical procedures.¹⁰⁻¹³

Table 29.4—Wavelengths of Critical Absorption Limits,¹⁵ in X.U.*

Atomic no.	K	L _I	L _{II}	L _{III}	M _I	M _{II}	M _{III}	M _{IV}	M _V
83 Bi	136.5 (136.8)	772.9 (775.9)	784.8 (787.8)	916.0 (922.1)	3062	3306	3819 (3893)	4542 (4568)	4731 (4763)
88 Ra	119.1	644.5	671.0 (670)	800.0 (802)	2561	2760	3248	3793	3975
89 Ac	116.0	625.8	650.9	779.7	2469	2665	3148	3673	3852
90 Th	112.0 (112.7)	606.4 (603.9)	630.5 (629.3)	758.6 (760.0)	2389 (2388)	2568 (2571)	3043 (3062)	3557 (3550)	3734 (3722)
91 Pa	110.2	587.6	611.0	738.2	2305	2483	2955	3432	3607
92 U	107.3 (106.6)	571.0 (568.0)	593.5 (591.3)	720.6 (720.8)	2231 (2228)	2401 (2385)	2870 (2877)	3327 (3327)	3500 (3491)
93 Np	104.6	554.8	576.6	703.6	2160	2323	2788	3226	3398
94 Pu	102.1	538.0	559.0	685.3	2086	2248	2710	3118	3287
95 Am	99.6	521.9	542.2	667.7	2021	2171	2626	3026	3194
96 Cm	97.2	507.4	527.0	652.5	1953	2102	2554	2938	3104

* Where two values are given, the one in parentheses is a known experimental value for comparison.

For quantitative chemical analysis, comparison of the intensities of the x-ray lines of the sample with those of a standard is made. As in all types of spectroscopic work, precautions must be observed in making the comparisons. The lines to be compared should be relatively close together and should require about the same degree of excitation. If they are too far apart, it may be difficult to obtain equal exposure times, which is an essential factor. Care must be observed to avoid ghost lines when the crystal is rotated. The effects of absorption of the x radiation by the material of the gelatin film may result in spurious changes which could cause false interpretations.

Use of x-ray spectroscopy as an analytical tool requires knowledge of the wavelengths, excitation voltages, relative intensities, and glancing angles for the lines of the elements being tested. This information for the commonly known elements is recorded in many standard reference works such as Siegbahn,¹⁰ Mark,¹² and Compton and Allison.¹⁴ For the heaviest elements, 83 to 96, inclusive, these data have been recalculated and extended by Monk and Allison;¹⁵ they are summarized in Tables 29.4, 29.5, 29.6, and 29.7. The x-ray spectra of the last-row elements are also discussed by Russell.¹⁶

Table 29.5—Critical Excitation Voltages, in Kilovolts¹⁵

Atomic no.	K	L _I	L _{II}	L _{III}	M _I	M _V
83 Bi	90.2	16.3	15.7	13.4	4.02	2.59
88 Ra	103.5	19.1	18.4	15.4	4.81	3.10
89 Ac	106.4	19.7	18.9	15.8	4.99	3.20
90 Th	109.5	20.4	19.6	16.2	5.16	3.31
91 Pa	112.0	21.0	20.2	16.7	5.35	3.42
92 U	114.7	21.7	20.9	17.1	5.53	3.53
93 Np	117.9	22.2	21.4	17.5	5.70	3.63
94 Pu	120.9	22.9	22.1	18.0	5.91	3.75
95 Am	123.9	23.6	22.7	18.4	6.10	3.86
96 Cm	126.9	24.3	23.4	18.9	6.31	3.97

Table 29.6 —Wavelengths, in X.U., and Intensities of Emission Lines in the K Series¹⁵

Atomic no.	K α_1 (intensity 100)	K β_1 (intensity 35)
83 Bi	160.4	142.0
88 Ra	140.2	123.6
89 Ac	136.3	120.4
90 Th	132.3	116.9
91 Pa	129.4	114.4
92 U	126.4	111.9
93 Np	122.9	108.7
94 Pu	120.0	106.1
95 Am	117.0	103.5
96 Cm	114.3	101.1

Table 29.7—Wavelengths, in X.U., and Intensities of Some Emission Lines in the L Series¹⁵

Atomic no.	L β_3	L β_1	L β_4	L η	L α_1	L α_2	L χ
Intensity	(3.3)	(40.5)	(3.2)	(0.83)	(100)	(11)	(2.4)
83 Bi	936.7	950.0	975.0	1056	1141	1153	1314
88 Ra	802	812	838	906	1001	1013	1163
89 Ac	788	789	815	882	978	990	1141
90 Th	753	764	792	853	954	966	1113
91 Pa	731	741	767	829	928	940	1087
92 U	709	719	746	804	909	921	1065
93 Np	690	699	726	784	887	900	1045
94 Pu	668	678	704	761	866	878	1022
95 Am	648	658	684	738	844	856	999
96 Cm	630	639	666	719	826	839	982

Analysis of uranium in the presence of iron, copper, chromium, and manganese has been evaluated.¹⁷⁻¹⁹ The L spectrum was employed for uranium since the excitation voltage for the uranium K radiation (113,000 volts) was too great for the apparatus used. For the elements mixed with uranium the K radiation is more desirable.

It was found that since the bromine K-absorption edge occurs on the long-wavelength side of the uranium $L\alpha_1$ line, a marked increase in background results. Increased exposure time resulted only in a heavier background.

Table 29.8—Evaluation of the X-ray Spectrograph for the Quantitative and/or Qualitative Determination of Uranium¹⁸

Film	U/Fe by wt.	Applied voltage	Rotation range, deg	Current, ma	Exposure time, hr	Remarks
T-3	Pure U_3O_8	15,000	5 to 22	10	2	$U L\alpha_1$, weak
T-4	1/1	15,000	5 to 22	10	2	$U L\alpha_1$, not visible
T-6	1/1	21,600	5 to 22	10	2	$U L\alpha_1$, strong
T-7	1/10	21,900	5 to 22	10	2	$U L\alpha_1$, medium
T-9	1/100	27,000	5 to 22	10	2	$U L\alpha_1$, weak
T-10	1/1,000	31,200	5 to 22	10	3	$U L\alpha_1$, weak

Sodium chloride crystals were found to be the most suitable from the standpoint of reflectivity and resolving power. It was found that potassium bromide, because of its greater instability, is less desirable than sodium chloride as the reflecting crystal.

One part of uranium in 1,000 parts of iron may be detected as indicated in Table 29.8. Cauchois^{20,21} points out that x-ray emission spectrum analysis is more satisfactory than x-ray absorption analysis. This work indicates that the amount of uranium per part of palladium, platinum, or boron ranges from 10^{-4} to 10^{-3} .

14. X-RAY ABSORPTION

For the detection of the main content of containers that could not be opened conveniently, Rainwater et al.²² developed a procedure employing the absorption of x rays. This is an extension of methods used for the examination of metal coatings.³ It was found that precise voltage control was necessary. The method was capable of detecting 0.1 g/sq cm of uranium under the condition used. Reference is made to the original article for details.

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